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A Program of Field Measurements

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TOXIC CHEMICALS IN THE ENVIRONMENT: A PROGRAM OF FIELD MEASUREMENTS

by

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ABSTRACT

An environmental mobile laboratory was instrumented and employed to perform a series of eight field studies of 1-to-3 weeks duration during which around-the-clock measurements of a large number of organic chemicals were performed in six United States cities under a variety of meteorological conditions. Field studies involved on-site analysis of 29 organic chemicals, many of which are mutagens or suspect carcinogens. Chemicals measured included chlorofluorocarbons, halomethanes, haloethanes, halopropanes, chlorinated alkenes, aromatic hydrocarbons, organic nitrogen compounds and aldehydes. The measured data are reported as mixing ratios and interpreted in the context of their mean diurnal behavior and chemical removal rates. Data tapes have been provided to the U. S. Environmental Protection Agency. Except for aromatic hydrocarbons and aldehydes, average concentrations of measured species were in the 0-to-5 ppb range. The average concentration range for aromatics and aldehydes was in the 0-25 ppb range. Maximum measured concentrations were typically 5 to 10 times the mean values. Typical diurnal profiles showed highest concentrations in the night and early morning hours. Minimum values observed in the afternoon were probably due to deep vertical mixing. San Jose studies clearly showed the effect of meteorology with mean concentrations rising 4 to 7 times normal values under stagnant conditions. Ambient data suggests that aldehydes are significantly less abundant in winter. Interpretation of aromatic hydrocarbon data from Southern California showed that the prevailing hydroxyl radical concentrations of 2.6×10^6 molec.cm^{-3} in February are not significantly different from values determined for summer. Analysis of historic data further suggests that the concentrations of benzene (the dominant toxic chemical in ambient air) have declined by a factor of about 10 in the ambient air of Southern California over the last two decades.

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SECTION 1

INTRODUCTION

Over the last three decades large amounts of a growing number of synthetic organic chemicals have been released into the ambient environment. In many cases, virtually all of the synthetic organic chemicals produced are released into the environment as a necessary result of use. Urban atmospheres contain a complex mixture of a large number of chemicals, many of which are known to be toxic at concentrations significantly higher than those encountered in typical ambient atmospheres. The degree to which the general ambient environment contributes to human cancer is a matter of both active research and debate. A report from the Office of the U.S. Surgeon General concluded that "toxic chemicals are adding to the disease burden of the United States in a significant, although as yet not precisely defined way" (U.S.S.G, 1980). The process of understanding the risks associated with exposure to potentially hazardous chemicals requires a determination of the ranges of concentrations that can be found in the ambient air.

This study was initiated primarily to measure the atmospheric concentrations of a variety of potentially hazardous gaseous organic chemicals* at selected urban locations under varying meteorological and source-strength conditions. This study complements and extends a similar study previously completed (Singh et al, 1983e). These chemicals were sampled and analyzed on-site, using a suitably outfitted mobile laboratory. The overall program of analytical methods development, field measurements, data collection, and data analysis is expected to provide information that will permit a better assessment of the atmospheric abundance and chemistry of this potentially harmful group of chemicals.

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*The term "hazardous chemicals" as used here is not intended to imply that a proven human health hazard exists. In most cases, toxicity studies are incomplete or inconclusive, and involve extrapolation of animal data to humans.

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16. ABSTRACT

A series of field measurements was carried out in six U.S. cities to assess the magnitude and variability of the concentration of twenty-nine potentially toxic air pollutants. The measurements were conducted on a 24-hour-per-day basis for periods of 1 to 3 weeks in each the following cities: Philadelphia, PA; Staten Island, NY; Downey (Los Angeles), CA; Houston, TX; Denver, CO; and San Jose, CA. Three separate periods of sampling were conducted in San Jose during different seasons of the same year. The chemicals which were measured included chlorofluorocarbons, halomethanes, haloethanes, halopropanes, chlorinated alkenes, aromatic hydrocarbons, organic nitrogen compounds, and aldehydes. For most species average concentrations were less than 5 parts per billion (v/v). Aldehydes and aromatics were more plentiful, but they still averaged less than 25 ppb. Maximum measured concentrations were typically 5 to 10 times the mean values. The data were analyzed and compared with historic data in order to examine for trends. Variations associated with meteorological influences were so great as to mask any potential seasonal or longer trends which may have been present in the limited data set available in this and a previous study. Diurnal patterns in the distribution of aromatic hydrocarbons in southern California suggest that, even in February, hydroxyl radical concentrations in the lower troposphere may reach 2.6×10^6 molecules cm^{-3}.

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SECTION 2

OVERALL OBJECTIVES

The major objective of this study was to perform a series of ambient field experiments in which atmospheric concentrations of a variety of selected hazardous organic chemicals were to be measured on around-the-clock basis, at a variety of urban locations, under varying meteorological conditions, and in different seasons.

To accomplish the above objective, analytical procedures were developed and a mobile environmental laboratory was equipped to perform onsite analysis of selected trace chemicals. Eight field experiments were performed in six cities to develop a reliable data base which could be used to better understand the atmospheric concentrations diurnal and seasonal behavior of these chemicals. These data are processed and interpreted in the context of sources, sinks, and the chemistry of the molecules. The effect of season and meteorological conditions was investigated.

SECTION 3

ANALYTICAL METHODOLOGY

Many of the procedures used here have already been described in Singh et al (1983e), and are therefore described only briefly. Table 1 lists the chemicals that were measured during this study. As has been reported (Helmes et al, 1983; Singh et al, 1982), most of these chemicals are mutagenic, carcinogenic, or can form products in the air that have these properties.

FIELD INSTRUMENTATION

Because of problems associated with surface reactions, it is widely recognized that the integrity of an air sample is best maintained when only nominal amounts of air samples are collected, and the time between collection and analysis is kept to an absolute minimum. Our on-site field analysis program was devised to meet these requirements. Table 2 summarizes the equipment that was available in our mobile laboratory for the conduct of this study. This laboratory was air-conditioned for temperature control, and operated on a 220-V, 80-A circuit. Provision was also made for operating on 110-V input. A 200-m electrical cord was always used to station the laboratory away from the electrical source or power pole. The sampling manifold was all stainless steel with a variable inlet height. (In all cases, the sampling manifold was adjusted to be higher than nearby structures: A typical manifold inlet height was 5 m above ground.) For pumping and pressuring air samples, a special stainless-steel metal bellows compression pump (Model MB 158) was always used. For the analysis of aldehydes, surface air was sampled in an all-glass apparatus.

EXPERIMENTAL PROCEDURES

For all of the halogenated species and organic nitrogen compounds shown in Table 1, electron-capture detector (ECD) gas chromatography (GC) was the primary means of analysis. The aromatic hydrocarbons were measured using flame-ionization detector (FID) gas chromotography (Singh et al, 1985b).

TABLE 1. LIST OF CHEMICALS MEASURED IN THIS STUDY

Measured Chemicals
CHLOROFLUOROCARBONS:
Trichlorofluoromethane (F-11)
Dichlorodifluoromethane (F-12)
Trichlorotrifluoroethane (F-113)
Dichlorotetrafluoroethane (F-114)
HALOMETHANES:
Methyl chloride
Methyl bromide
Methyl iodide
Methylene chloride (Dichloromethane)
Chloroform (Trichloromethane)
Carbon tetrachloride
HALOETHANES AND HALOPROPANES:
Ethyl chloride
1,2-Dichloroethane
1,2-Dibromoethane
1,1,1-Trichloroethane
1,2-Dichloropropane
CHLOROALKENES:
Trichloroethylene
Tetrachloroethylene
AROMATIC HYDROCARBONS:
Benzene
Toluene
Ethyl benzene
m/p-Xylene
o-Xylene
3/4-Ethyl toluene
1,3,5-Trimethyl benzene
1,2,4-Trimethyl benzene
OXYGENATED SPECIES:
Peroxyacetylnitrate (PAN)
Peroxypropionylnitrate (PPN)
Formaldehyde
Acetaldehyde

TABLE 2. ENVIRONMENTAL MOBILE LABORATORY INSTRUMENTATION*

Instrument	Features	Analysis
Perkin Elmer 3920 GC1	2 ECD†, 1 dual FID‡	Trace constituents
Perkin Elmer 3920 GC2	2 ECD, 1 dual FID	Trace constituents
Perkin Elmer 3920 GC3 (capillary column GC)	2 ECD, 1 dual FID	Trace constituents
Coulometric dual EC-Gc	Coulometric ECD	Halocarbons, PAN, PPN, $COCl_2$; calibration
Spectraphysics HPLC 8700 (variable wavelength SP3400 detector)	HPLC§	Aldehydes
Beckman 6800	FID	$CO-CH_4$-THC
Horiba AIA-24	NDIR**	CO, CO_2
Bendix 8101-B	Chemiluminescent	NO, NO_2
Monitor Labs Model 8440E	Chemiluminescent	NO and NO_2
Dasibi Model 1003 AH	Photometric principle	O_3
AID Model 560	Chemiluminescent	O_3
Bendix 8002	Chemiluminescent	O_3
Eppley pyranometer		Solar flux
Eppley UV radiometer		Ultraviolet radiative flux
Miscellaneous meteorological equipment		Wind speed, wind direction, temp, pressure, dew point, relative humidity
Auto Lab IV Data System (No. 1)		GC data
SP-4000 Multichannel Data System (No. 2)		GC data
HP-3390 printer plotter		
Digitem Data System (No. 3)		All continuous air quality and meteorological data

*Note: Sampling of all trace organics is performed from a stainless-steel manifold. A Teflon® manifold is used for inorganics (e.g., O_3, NO, NO_x). Finnigan 3200 GC/MS available to this project at SRI.

†Electron capture detector.

‡Flame ionization detector.

§High performance liquid chromatograph.

**Nondispersive infrared.

Formaldehyde and acetaldehyde were measured by analyzing the 2,4 dinitrophenylhydrazine derivatives formed by reaction of 2,4 dinitrophenylhydrazine (DNPH) with aldehydes, using high-performance liquid chromatographic (HPLC) methods (Kuwata et al, 1979; Kuntz et al. 1980; Fung and Grosjean, 1981; Salas and Singh, 1985).

All six GC channels were equipped with stainless-steel sampling valves, and could be operated either with a direct sampling loop or with a preconcentration trap. In no instance was a sample size of greater than 1 liter used: In most cases, sample volumes of 500 ml or less were satisfactory. Sample preconcentration was conducted on a 4-inch-long bed of 100/120 mesh glass beads packed in 1/16-inch diameter stainless-steel tubing maintained at liquid oxygen temperature. The glass beads could be replaced with an equivalent length of SE-30 packing (3 percent SE-30 on 100/120 mesh acid-washed chromosorb W) or glass wool, with completely satisfactory results. Desorption of chemicals from the preconcentration traps was accomplished by holding the trap at boiling-water temperature and purging with carrier gas. Additional details have been earlier provided by Singh, et al (1979a, 1983e).

Two types of sampling procedures were employed. During the first five field programs, an on line 2-liter SUMMA^{R} polished stainless steel canister was pressurized to 32 psi during a 3 to 5 minute period, and this air was used for GC analysis.

During the last 3 field programs (at San Jose, CA), a different sampling arrangement was used in order to provide 2-hourly integrated samples (Figure 1). A 6-liter SUMMA^{R} polished stainless steel canister was slowly pressurized to approximately 27 psi, using a metal bellows pump followed by a pressure relief valve (set at 28 psig), and a mass flow controller PFD Model 914 set at 150 cc/min. Prior to sampling, the canister was evacuated by a vacuum pump to less than 0.08 atm. It was then slowly filled (at 150 cc/min) to approximately 27 psig. In this manner, about 18 liters (STP) of air were pumped into the 6-liter canister over a 2-hour period. Because the canister was evacuated to 0.08 atm, less than 3 percent of a previous sample was carried over into the next sample introduced into that canister. The sampling system was configured with three canisters and switching between them and between vacuum

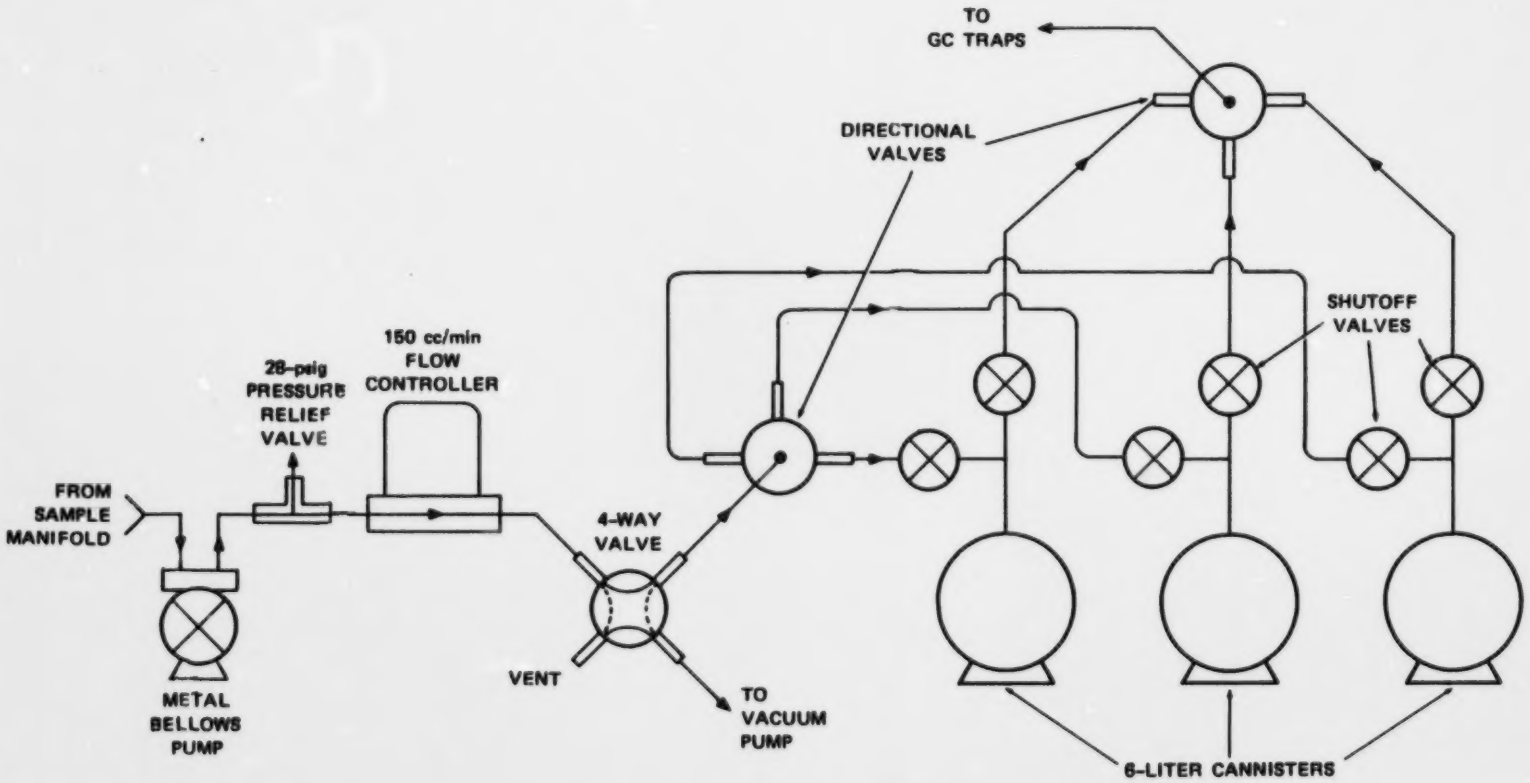

Figure 1. Assembly for a 2-h integrated air sample collection in 6-liter stainless steel canisters.

or pressure pumps was accomplished by means of stainless steel directional valves. The pressure relief valve allowed most of the flow (approx. 10 ℓ /min) to be vented upstream of the flow controller. In this way, the metal bellows pump was kept continuously flushed and cool, preventing degradation or contamination of the sample. Two tests were conducted to check for contamination from this pumping arrangement. One used pure N_2 from a cylinder instead of sample air. Analyses on all GC channels showed no halocarbon or aromatic contamination added by the metal bellows pump, flow controller, or other components in the sampling line. A second test was conducted using a 35-liter canister pressurized to 35 psig with ambient air. Analyses of the air sample on all GC channels before and after passage through the sampling train showed no change in any of the chemicals of interest.

The preconcentration and analysis procedure was identical in both cases. Tests were performed to ensure that no contamination occurred during this sampling procedure. The volume preconcentrated (dry basis) was measured by noting the pressure change in a vessel of known volume connected to the trap exit. A high precision pressure gauge (±0.05 psi) was used to monitor this pressure. It was determined that for sample volumes of 200 ml or more, an accuracy of ± 2 percent could be easily obtained.

Table 3 summarizes the routine methods used for the analysis of trace species. The GC and the HPLC conditions used are both stated. Because of the dominant water response of the ECD, a pre-column Nafion^R drier was inserted to remove water for halocarbon analysis. No drier was used for the analysis of aromatic hydrocarbons, PAN and PPN. The latter two do not require any preconcentration step, and were measured with a direct 5-ml air injection. For the aldehyde DNPH-HPLC analysis, the technique described by Kuntz et al (1980) was employed. The sampling reagent was prepared by dissolving 0.25 g of purified DNPH in 1.0 liter of HPLC-grade acetonitrile, and adding 0.2 ml of concentrated sulfuric acid to this solution. DNPH was purified by repeated recrystallization (at least three times) from HPLC-grade acetonitrile. A 7-ml aliquot of this reagent solution was transferred into a bubbler and cooled with the help of an icewater Dewar flask. During ambient sampling (60 liters), an air-flow rate of 0.5 liter/min was maintained for a typical sampling period of two

TABLE 3. ANALYTICAL CONDITIONS FOR THE ANALYSIS OF SELECTED TOXIC CHEMICALS

GC or HPLC Column				Detector		Typical Carrier Flow Rate (ml/min)	Typical Sample Size (ml)	Remarks
No.	Description	Temp. (°C)	Species Measured	Type	Temp. (°C)			
1	6 ft x 1/8 in, SS,* 20% SP2100, 0.1% DC 1500 on 100/120 mesh Supelcoport	45	$CHCl_3$; CH_3CCl_3; CCl_4; cis-$CHClCHCl$; C_2HCl_3; $CH_2ClCHCl_2$; CH_2BrCH_2Br; C_2Cl_4; CH_2ClCCl_3; $CHCl_2CHCl_2$; $CH_2ClCHClCH_3$	Electron capture	275	40	500	Precolumn Nafion® water trap
2	33 ft x 1/8 in, Ni, 20% DC 200 on 80/100 mesh Supelcoport	45	CH_3Cl; CH_3Br; CH_2CCl_2; CH_3I; CCl_3F; CCl_2F_2; $CClF_2CCl_2F$; $CClF_2CClF_2$; C_2H_5Cl; CH_2Cl_2; CH_2ClCH_2Cl; CH_3CCl_3; CCl_4; C_2HCl_3; C_2Cl_4	Electron capture	275	25	500	Precolumn Nafion® water trap
3	6 ft x 1/8 in, SS, 10% N, N, -bis (2-cyanoethyl) Formamide on Chromosorb P (acid washed)	65	C_6H_6; $C_6H_5CH_3$; m/p/o-$C_6H_4(CH_3)_2$; 3/4-$C_6H_4C_2H_5$; 1,3,5 $C_6H_3(CH_3)_3$; 1,2,4 $C_6H_3(CH_3)_3$	Flame ionization	275	45	500	No water trap
4	10 in x 1/4 in, Teflon, 5% CS 400, on 60/80 mesh Chromosorb W (acid washed	30	PAN, PPN	Electron capture	30	60	5	No water trap; direct injection
5	1 ft x 1/4 in SS, sphersorb ODS-10	30	HCHO, CH_3CHO	Variable wavelength detector set at 360 nm	30	1.5	0.01	Isocratic mode, 36% H_2O, 64% acetonitrile SP mode 8700, SP 3400 detector

*Stainless Steel

hours. The sampling reagent was added to compensate for any evaporative losses. After sampling, a 2.0-ml aliquot of the reagent solution was transferred into a heavy-walled Teflon-capped reaction flask, warmed at 75° for 20 minutes, and then cooled to room temperature. The DNP-hydrazone derivatives were analyzed with a Spectra Physics HPLC (Model 8700) equipped with a 1 ft x 1/4 inch SS Spherosorb ODS-10 column, and a variable-wavelength-detector (Model 3400) set at 360-nm wavelength. The HPLC was used in an isocratic mode with a solvent flow rate of 1.5 ml/min. A 36 percent H_2O, 64 percent acetonitrile, solvent gave the best resolution of the two hydrozones of interest. A 10-µl sampling loop was used for HPLC analysis. Typical analysis time was less than 10 minutes.

The identity of trace constituents was established by using the following criteria:

- Retention times on multiple GC columns (minimum of two columns)
- EC thermal response
- EC ionization efficiency

Details of these comparisons for halocarbon species, organic nitrogen compounds, and aromatic hydrocarbons have already been published (Singh et al, 1979a; 1983e).

CALIBRATIONS

Primary Standards

Calibrations for all species were performed using three basic methods:

- Permeation tubes
- Multiple dilutions
- Gas-phase coulometry.

As reported earlier (Singh et al, 1979a; 1983e), permeation tubes provide a reliable means to generate low-ppb primary standards for a significant number of chemicals listed in Table 1. Permeation tubes (8- to 10-cm long) constructed from standard FEP or TFE Teflon^R tubing of varying thicknesses, were obtained commercially for many trace constituents of interest. Each permeation tube was contained in a specialized glass holder. Based on our previous

experience, we concluded that some permeation tubes could operate satisfactorily only at high temperatures. Therefore, two temperature baths maintained at 30.0°C ± 0.05°C and 70.0°C ± 0.1°C were installed. The 30°C bath was a water bath, and the 70°C bath was an oil bath (later replaced by a solid aluminum block machined to hold glass chamber inserts). All permeation tubes were contained in specialized holders and were purged continuously with a prepurified gas (helium, air, or nitrogen) flowing at 50 to 80 ml/min. Permeation tubes were weighed approximately once a week on a semi-micro (10^{-5}g) balance. These weighings were done before, during, and after the field experiments. The constancy of the permeation rate over a period of many months could be established. A large-volume mixing chamber was installed at the permeation tube exit to allow for complete mixing. Samples were withdrawn from the mixing chamber using all-glass syringes. Our previous results (Singh et al, 1983e) showed that the permeation tubes demonstrated excellent linearity of permeation rates, and proved to be a reliable means to generate primary standards. Table 4 shows permeation rate data for a variety of chemicals of interest. Most of these permeation tubes can be used to prepare standards directly at parts per billion (ppb) concentration levels. Batch dilutions were carried out to reduce these concentrations by a factor of 10^2 to 10^3. These were performed by injecting a known volume (typically 10.0 ml) of the high concentration mixture into an evacuated precleaned electropolished stainless steel container of 1- to 5-liter size, followed by pressurization with dilute gas to 40 psi. Over a wide range of concentration levels of low ppb's and low ppt's (parts per trillion), the frequency-modulated ECDs that we used were linear. The linearity of the FID over a much larger concentration range is well known.

In addition to permeation tubes, standards were obtained from Scott-Marrin (Riverside, California). These were obtained at higher concentrations (5 to 10 ppm) for long-term stability. Table 5 lists the chemicals, the standard concentrations, and the cylinder materials. All of the chemicals were stored in aluminum cylinders except those containing CH_3Cl, which were contained in stainless-steel cylinders. Extreme care was required in selecting cylinder materials; some of the chemicals (e.g., methyl chloride) form unknown chemical complexes that might react explosively with aluminum (Private

TABLE 4. PERMEATION RATE DATA FOR GENERATING PRIMARY STANDARDS

Compound	Permeation Tube Number or I.D.	Temperature (°C*)	Permeation Rate		Quality†
			ng/min	ppb/l/min (25°C, 1 atm)	
HCHO	MET8	70.0	326	266	F
CH_2=CHCHO	2356	30.0	969	423	E
CH_2OCH_2	1908	30.0	1120	618	E
CH_3CHO	MET9	30.0	3300	1837	E
CH_3COCH_3	MET10	30.0	615	260	G
C_2H_5CHO	MET11	30.0	2604	1100	E
C_6H_5CHO	MET12	30.0	95	23	F
CCl_2F_2 (F12)	6138	30.0	615	123	E
CCl_3F (F11)	1911	30.0	1680	299	E
$CHCl_2F$ (F21)	2347	30.0	942	224	E
$CHClF_2$ (F22)	2348	30.0	80	23	E
GCl_2FCClF_2 (F113)	1238	30.0	715	93	E
$CClF_2CClF_2$ (F114)	2345	30.0	6254	894	E
CH_3Cl	2355	30.0	1915	927	E
C_2H_5Cl	2350	30.0	480	182	E
CH_2CHCl	2352	30.0	1270	497	E
$ClCH_2CH$=CH_2	7497	30.0	142	45	E
CH_3Br	1893	30.0	2477	638	S
CH_3I	1239	30.0	109	19	G
CH_2CI_2	2354	30.0	523	150	E
(cis) CHClCHCl	1939	30.0	2564	646	E
(trans) CHClCHCl	1898	30.0	1696	428	E
CCl_2CH_2	1897	30.0	731	184	G
CH_2ClCH_2Cl	1907	70.0	2622	648	E
CH_2ClCH_2Cl	1899	30.0	125	31	G
$CHCl_2CH_3$	2353	30.0	71	18	G
$CH_2ClCHClCH_3$	MET1	70.0	2456	531	E
(trans) CHCl=$CHCH_2Cl$	MET2	70.0	7806	1720	E
$COCl_2$	2351	30.0	942	233	E
$CHCl_3$	1229	30.0	174	36	G
C_2HCl_3	1253	30.0	314	58	E
CCl_3CH_3	1896	70.0	980	179	E
CCl_3CH_3	1589	70.0	3450	632	E
$CHCl_2CH_2Cl$	1901	30.0	129	24	G
CCl_4	1894	70.0	1983	315	F
C_2Cl_4	1902	70.0	3352	494	E
C_2Cl_4	1590	30.0	706	104	E
CH_2BrCH_2Br	1237	70.0	1220	160	E
$CHBr_3$	1895	70.0	1316	127	E
C_6H_5Cl	MET3	70.0	4507	980	E
$C_6H_5CH_2Cl$	MET4	70.0	1528	295	E
o-$C_6H_4Cl_2$	MET5	70.0	1359	226	E
m-$C_6H_4Cl_2$	MET6	70.0	2515	418	E
p-$C_6H_4Cl_2$	MET7	70.0	3571	593	E

Note: All permeation tubes were given a 2 week or longer conditioning time.

*Temperature maintained to ±0.05°C.

†E=Excellent (errors in permeation rate < ±10%); G=Good (errors in permeation rate < ±15%); F=Fair (errors in permeation rate < ±25%).

TABLE 5. PPM LEVEL PRIMARY STANDARDS IN AIR*

Standard and Compound†	Concentration (ppm)	Long-term Stability‡ (2-year period)	Cylinder	
			Type	Size (ft^3)
S1				
1,1,1 Trichloroethane	5.0	E		
Carbon tetrachloride	5.2	E		
1,2 Dibromoethane	5.0	E	Aluminum	30
Hexachloroethane	0.8	U		
S2				
Monochlorobenzene	5.0	P	Aluminum	150
o-Dichlorobenzene	5.0	P		
S3				
Benzene	5.0	E	Aluminum	150
Toluene	5.0	E		
S4				
Methyl chloride	10.0	E		
Methylene chloride	10.0	E	Stainless steel	30
1,2 Dichloroethane	10.0	E		
S5				
Trichloroethylene	10.0	E		
Tetrachloroethylene	10.0	E	Aluminum	30
Chloroform	10.0	E		
S6				
Ethane	4.07	E		
Propane	5.03	E	Aluminum	150
n-Butane	4.95	E		
S7				
Methyl chloride	10.0	E/S		
Methyl bromide	10.0	E/S	Stainless steel	30
Methyl iodide	5.0	E/S		

*Obtained on order from Scott-Marrin, Inc., Riverside, California.

†For all of these chemicals (except C_6H_6 and $C_6H_5CH_3$) satisfactory permeation tubes were also operational. Therefore, a majority of these standards were used more as secondary standards than as primary ones. For aromatic hydrocarbons, the Scott-Marrin standards were used as primary standards.

‡E: Excellent; P: poor; U: unknown; E/S: Excellent over the short term; long-term tests have not been made.

Communication--Scott-Marrin Inc.). Chlorobenzenes deteriorated rapidly in these cylinders, other halocarbons and hydrocarbons were found to be extremely stable. The toluene response deteriorated at a slow rate of 3 percent per year. Benzene was much more stable and did not show any perceptible loss.

All of the commercially-obtained standards were rechecked with our permeation-tube standards when this was possible. The comparisons were found to yield excellent results (±10 percent). The aromatic hydrocarbon standards were checked for carbon response against those available from the National Bureau of Standards (NBS) and found to agree within ±5 percent. For other aromatic hydrocarbons, carbon response derived from benzene response was used.

PAN and PPN were measured with the help of a dual ECD gas phase coulometer according to the procedures described by Singh et al (1983d). It is estimated that this analysis is accurate to ±20 percent.

Secondary Standards

Except for the aromatic hydrocarbons, it was not possible to use primary standards during field operation. Therefore, an optimal scheme that depended on the use of secondary standards was devised.

A 35-liter and several 5-liter (as backups) SUMMA^{R} polished stainless-steel samplers were filled with urban air samples to a pressure of 35 to 40 psi. These were allowed to stabilize for one to two days and then analyzed by comparing them against the primary standards. The 35-liter pressurized secondary standard was then used for field operation: Each GC channel was calibrated one to two times a day with this secondary standard. The stability of nearly all species over a period of several days was found to be excellent (Singh et al, 1983e). Some species, such as PAN, PPN, and occasionally CCl_4, could not be stored for any reasonable length of time. This was not a serious hindrance since other chemicals could be used to ascertain the constancy of the ECD and the FID responses during field operations. All of the Scott-Marrin standards were also carried on board after these had been diluted to low-ppb levels. They were also used as secondary standards (in addition to

the collected air samples). The stability of the diluted Scott-Marrin cylinders (in polished 1- to 5-liter stainless-steel vessels) was found to be excellent. Analysis of these before field experimentation, during field studies, and after the completion of field studies did not show a change from the measurement precision under field conditions. In the case of aldehydes, all calibrations had to be performed in the field.

QUALITY CONTROL AND ASSURANCE

Two major factors were critical in establishing the quality of the acquired data: the accuracy of primary standards, and the precision and repeatability of measurements. As stated earlier in this section, the primary standards commercially obtained were compared with our permeation tubes, which can be routinely used to obtain reliable standards within errors of 10 percent. The aromatic hydrocarbon standards were compared with NBS propane standards and found to be accurate to within ±5 percent. The cross-calibrations between SRI-generated standards and Scott-Marrin standards typically resulted in differences of about ±10 percent or less. The use of secondary standards, at least on a daily basis, clearly demonstrated the excellent precision that was obtainable during field studies: The precision of reported field measurements is estimated to be better than ±15 percent. Because of the unavailability of standards at low concentrations, the overall accuracy of individual measurements cannot be ascertained. We estimate that in most cases the overall accuracy of data are within ±30 percent. This is established based on a number of audits performed by Northrop Services Inc. (NSI) under contract to EPA and utilizing somewhat different sampling and analysis techniques (Shepson and Kleindienst, 1986; Shepson et al, 1986). Figures 2-7 show a comparison of SRI and NSI data for chloroethane, benzene, toluene and tetrachloroethylene at the Philadelphia and San Jose sites. Comparisons with other chemicals could not be performed as these data were not available from NSI. Nevertheless, data for the four chemicals clearly show that the two methods track the concentration variability reliably, and the measured values agree within ± 30% over a wide concentration range.

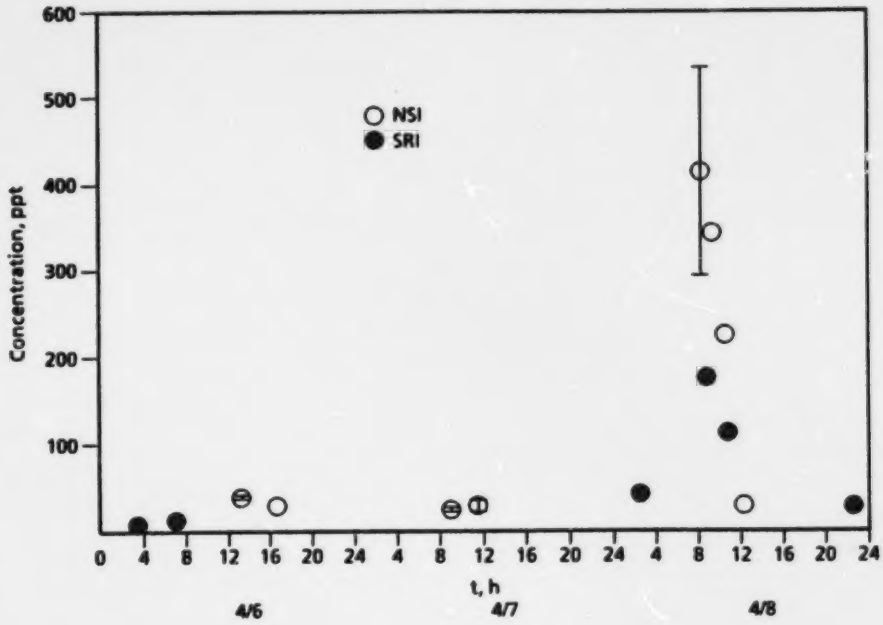

Figure 2. Chloroethane concentrations at the Philadelphia site as measured by SRI and NSI.

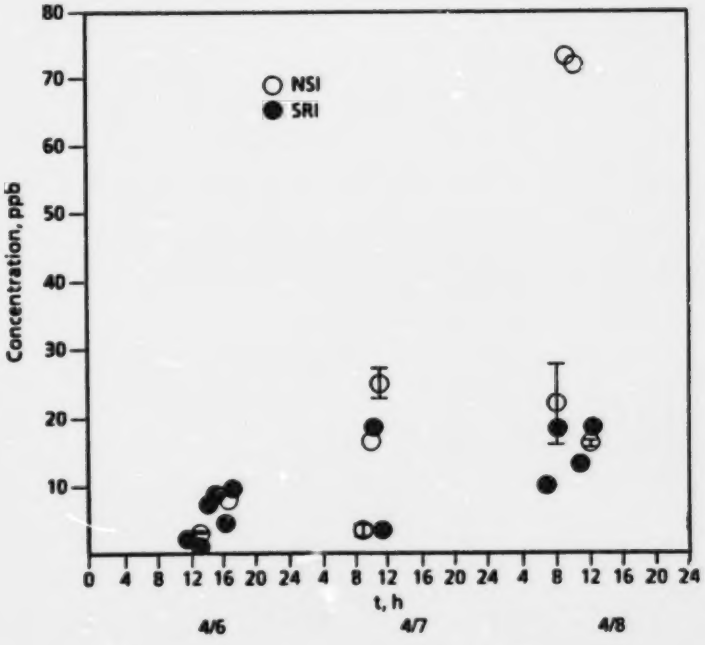

Figure 3. Toluene concentrations at the Philadelphia site as measured by SRI and NSI.

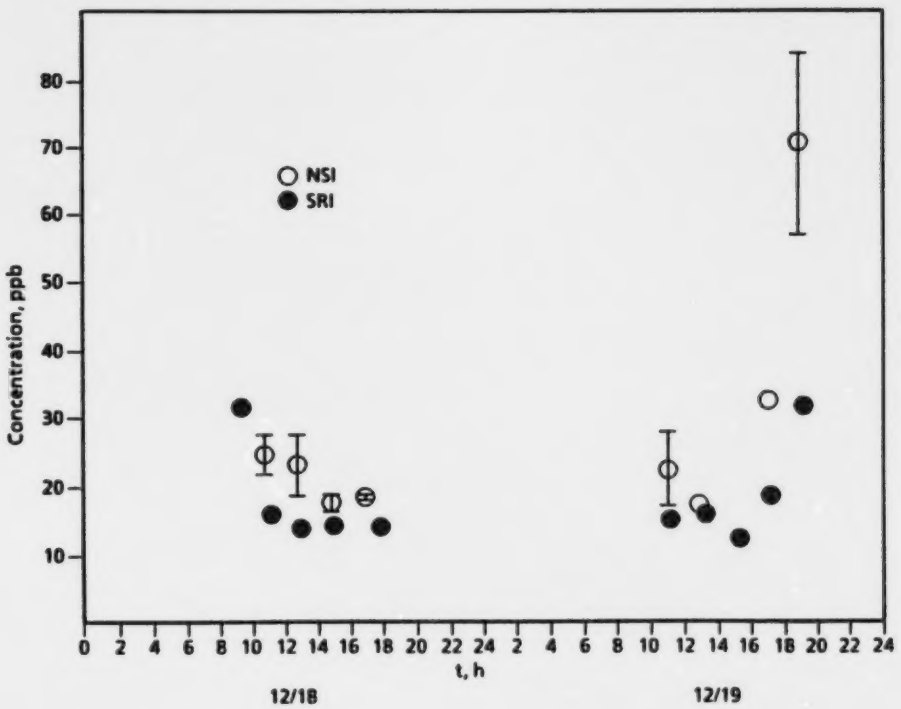

Figure 4. Toluene concentrations at the San Jose site as measured by SRI and NSI .

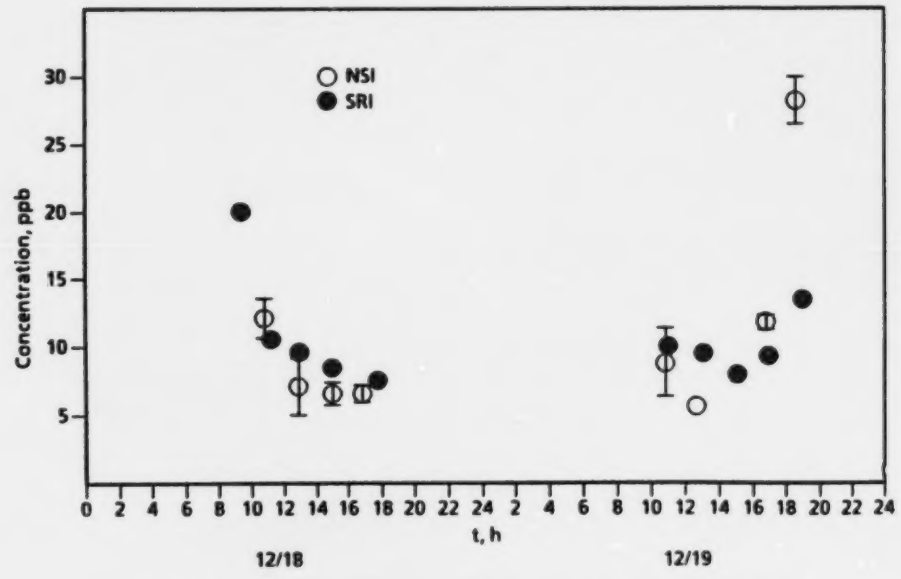

Figure 5. Benzene concentrations at the Philadelphia site as measured by SRI and NSI.

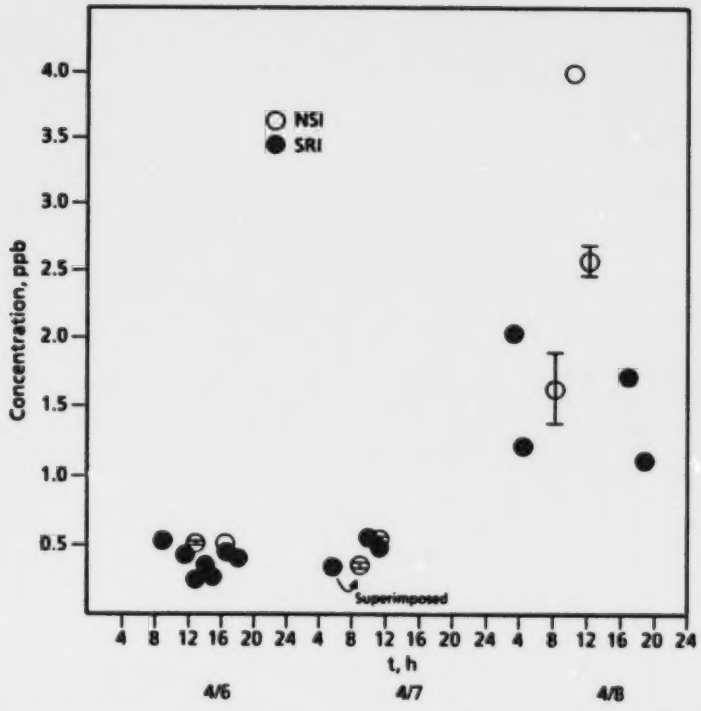

Figure 6. Tetrachloroethylene concentrations at the Philadelphia site as measured by SRI and NSI.

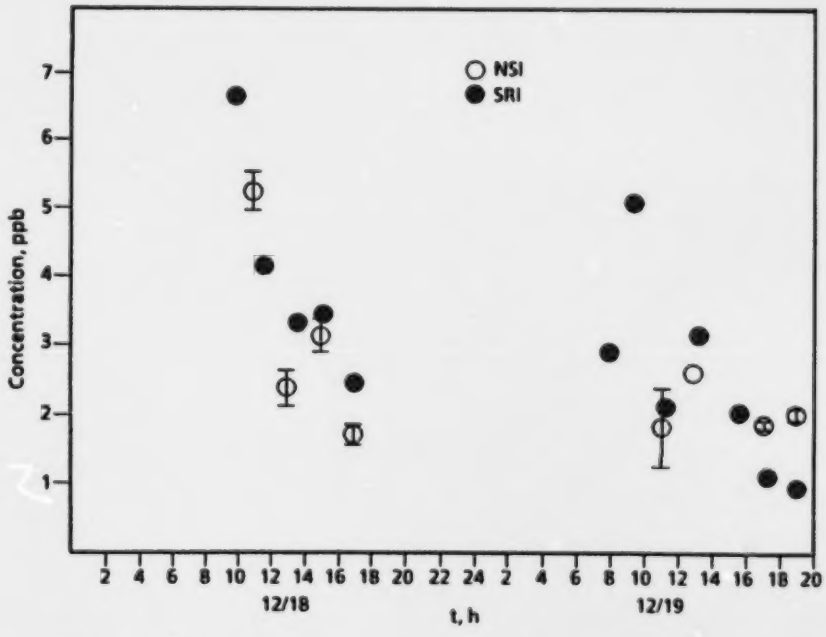

Figure 7. Tetrachloroethylene concentrations at the San Jose site as measured by SRI and NSI.

SECTION 4

FIELD MEASUREMENTS

Eight field studies were performed in six select urban environments in the continental United States. The sites were chosen in consultation with the project officer and were located in the following cities:

- Philadelphia, Pennsylvania
- Staten Island, New York
- Downey, California
- Houston, Texas
- Denver, Colorado
- San Jose, California

Within the above cities, specific sites were chosen that represented an open urban area. Large point sources or topographical features that could affect the representativeness of the measurements were avoided. Every attempt was made to select sites that could be expected to be indicative of general pollution levels prevalent in the area. Practical constraints such as power and shelter availability also played a role in the selections of sites. It must be emphasized that only one site within each of the selected cities was monitored. The data collected here, while perhaps typical of general ambient environment, are truly representative only of the specific site monitored.

The site locations, and the periods of field measurements, are shown in Table 6. On the average each field study was of roughly two weeks duration, with a range of 1 to 3 weeks. Based on our past experience (Singh et al, 1982; 1983e), we believed that significant night and daytime differences were likely in the abundance of organic chemicals. Thus we concluded that despite the logistical difficulty, a 24-hour measurement schedule offered the most efficient means to collect the maximum amount of data needed to characterize the burden of toxic organic chemicals in the ambient air. In addition, night abundances of trace chemicals were likely to provide important information about the sources and sinks of measured species. Therefore, a 24-hour-per-day, seven-days-a-week measurement schedule was followed during all field programs.

TABLE 6. FIELD SITES AND MEASUREMENT SCHEDULE

Experiment No.	City	Experiment Period	Site Address
1	Philadelphia, PA	4-22 April 1983	Lycoming and Castor St.
2	Staten Island, NY	25 April - 1 May 1984	Wild Ave. and Victory Blvd.
3	Downey, CA	18-27 February 1984	7601 East Imperial Rancho Los Amigos Hospital
4	Houston, TX	9-17 March 1984	Mae St. and I-10 Frontage Road
5	Denver, CO	24 March - 1 April 1984	Marion and E. 51 St.
6	San Jose, CA	4-16 April 1985	Alma and Senter Road (San Jose Historic Museum)
7	San Jose, CA	12-24 August 1985	Alma and Senter Road (San Jose Historic Museum)
8	San Jose, CA	13-21 December 1985	Alma and Senter Road (San Jose Historic Museum)

The Philadelphia site was selected by the U.S. Environmental Protection Agency (EPA). This is among the few sites that were chosen in a preliminary attempt to establish a national toxic chemical monitoring network. The data presented here thus complements, and can be compared against, routine measurements that continue to be conducted at this site by the EPA. The next 4 sites (Staten Island, Downey, Houston, and Denver) represented sites that had been previously sampled in spring/summer months. (Downey was substituted for Los Angeles since the Los Angeles site was no longer available.) The purpose here was to revisit these sites in different seasons and years.

The San Jose site was selected because of great concern in the "Silicon Valley" area about exposure to chemicals used by the electronics industry. Many of the chemicals of concern were being measured in this study. Additionally it was felt that these data could prove to be of great value to the EPA Integrated Environmental Management Program (Hinman et al, 1985) that is being conducted in this area with a focus on water contamination. Prior to our studies there was a virtual absence of ambient air data from the Silicon Valley area.

Additionally, the three studies at the San Jose site offered an opportunity to look at seasonal differences in an area which is strongly influenced by prevailing synoptic conditions. The winter study in San Jose (Expt. No. 8) took place during an unusually strong high pressure weather system in which a large stagnant air mass covered most of the Western U.S. A low-level inversion trapped pollutants in the entire Santa Clara Valley, and drove carbon monoxide concentrations to the third highest levels on record (Bay Area Air Pollution Control District).

As was anticipated, these field studies encountered a wide range of weather and climatic conditions (stagnation, snow, rain, clear skies, etc.) and therefore should be extremely useful in establishing the ranges of concentrations encountered in the ambient air of a variety of urban atmospheres.

SECTION 5

ANALYSIS AND INTERPRETATION OF FIELD DATA

The data collected during these studies have been compiled, validated, and statistically treated. A computer-compatible master data file has been created. In addition to computer processing of field data, we have also analyzed data to study the diurnal variations that are typically observed. The data generated in this study, however, when further analyzed in the context of prevailing meteorology and source inventories, have the potential to add significantly to our knowledge of urban atmospheric chemistry.

Table 7 is presented to give a general idea of the yearly U.S. production, average emissions, and typical use patterns of important chemicals. A major source term for each of the chemicals has also been assigned, based on available information. Table 7 provides a preliminary basis for comparing the relative abundance of chemicals in the ambient atmospheres.

Statistical summaries of all field data are presented in Tables 8, 9, and 10. All concentrations are expressed in units of parts per trillion by volume (pptv $=10^{-12}$ v/v). Quantities tabulated are the means and standard deviations (one sigma), maximum and minimum conconcentrations, and the number of positive (nonzero) measurements as well as the total number of measurements performed. These statistics include all measured data. When the concentration was below our detectable limit, it was assigned a value of zero. In most cases values were below detection only infrequently (Tables 8-10). Additionally, plots of concentrations vs time and mean diurnal profiles have been constructed for all species, and some of these will be presented in the following sections. Average diurnal patterns were calculated by stratifying the data according to the sample collection time. Except for San Jose, all of the data from the complete sampling period were grouped according to the 3-hour interval (midnight to 3 a.m., 3 a.m. to 6 a.m., etc.) in which the sample was collected. Arithmetic means and standard deviations were calculated for each time interval and are plotted at the midpoint of the interval (at 1.5 hours, 4.5 hours, etc.) In the plots, the means are represented by a symbol, while the plus and minus one-sigma standard deviation values are shown as connected

TABLE 7. PRODUCTION, EMISSION AND USAGES OF SELECTED CHEMICALS

Compound	Source*	U.S. Production for Indicated Year† (million metric tons)	Emissions† (percent)	Usage and Remarks
Methyl chloride	A; N(O)	0.20 (1978)	5 - 10	85 percent of production used for manufacture of silicones and tetramethyl lead intermediates; large natural source (≥3 million tons/yr) identified in the ocean
Methyl bromide	A; N(O)	0.02 (1977)	≥50	Soil fumigant; oceanic source significantly larger than man-made emissions is possible
Methyl iodide	N(O)	≥0.0	-	A natural oceanic source of ≥0.5 million tons/yr is estimated
Methylene chloride	A	0.30 (1978)	80 - 90	55 percent of production used for paint removing and solvent degreasing
Chloroform	A	0.16 (1978)	5 - 10	Manufacture of fluorocarbon-22
Carbon tetrachloride	A	0.34 (1978)	5 - 10	Manufacture of fluorocarbons-11 and -12
Ethyl chloride	A	0.3 (1978)	25	85 percent consumed in the manufacture of tetraethyl lead
1,2 Dichloroethane	A	4.8 (1978)	≥2	87 percent used for vinyl chloride monomer synthesis; also used for the production of chlorethylenes and chloroethanes; about 0.4 million tons per year used for lead scavenging in automobiles
1,2 Dibromoethane	A	0.1 (1976)	5 - 25	Major gasoline additive for lead scavenging; also used as a fumigant
1,1,1 Trichloroethane	A	0.3 (1978)	≥95	70 percent of production used for metal cleaning; most other applications also result in direct release
Vinyl chloride	A	3.2 (1978)	2 - 5	Used for polymer synthesis
Vinylidene chloride	A	0.2 (1974)	2 - 5	Used for polymer synthesis
Trichloroethylene	A	0.14 (1978)	>90	70 to 80 percent used for metal cleaning
Tetrachloroethylene	A	0.33 (1978)	>90	60 percent used for dry cleaning and textile processing, another 15 percent used for metal cleaning
Monochlorobenzene	A	1.5 (1978)	>50	50 percent used in solvent applications, remainder in the production of nitrobenzene, DDT, diphanyl oxide
o-Dichlorobenzene	A	0.04 (1976)	>25	About 25 percent of production used in solvent applications
p-Dichlorobenzene	A	0.03 (1976)	>90	90 percent of production used for space deodorizing and moth control
1,2,4 Trichlorobenzene	A	0.01 (1973)	No data	70 percent used as a dye carrier and a herbicide intermediate
Benzene	A	5.0 (1978)	2 - 5	Auto exhaust is the major emission source; estimated U.S. total emissions approach 0.5 million metric tons per year
Toluene	A	4.2 (1978)	2 - 5	Auto exhaust is the major emission source; estimated U.S. total emissions approach 1 million metric tons per year
o-m-p Xylenes	A	2.9 (1978)	2 - 5	Auto exhaust is the major emission source; estimated total U.S. emissions approach 0.5 million metric tons per year
Formaldehyde	A, N	2.6 (1979)	-	Auto exhaust is a major primary source; significant secondary photochemical sources also exist. A major natural source from methane oxidation is likely.

*A=anthropogenic, N=natural, O=oceanic.

†Source: Singh et al. (1979a, 1980); U.S. Tariff Commission reports.

TABLE 8. ATMOSPHERIC CONCENTRATIONS OF MEASURED CHEMICALS FOR PHILADELPHIA AND STATEN ISLAND

Chemical Group and Species	Philadelphia 4-22 April 1983					Staten Island 25 April - 1 May 1983				
	PPTV					PPTV				
	Mean*	S.D.**	Maximum	Minimum	n/N†	Mean	S.D.	Maximum	Minimum	n/N
CHLOROFLUOROCARBONS:										
Trichlorofluoromethane (F-11)	369	182	1667	211	88/88	284	110	614	137	33/33
Dichlorodifluoromethane (F-12)	595	279	2474	340	88/88	566	269	1554	296	32/32
Trichlorotrifluoroethane (F-113)	--	--	--	--	--	--	--	--	--	--
Dichlorotetrafluoroethane (F-114)	41	88	616	10	76/76	24	13	80	10	31/31
HALOMETHANES:										
Methyl chloride	769	299	2883	348	91/91	654	280	1367	328	33/33
Methyl bromide	47	30	124	23	34/34	80	96	447	25	23/23
Methyl iodide	3	3	9	0.8	8/8	5	2	9	3	21/21
Methylene chloride (Dichloromethane)	622	559	3098	121	91/91	1109	1614	8868	243	34/34
Chloroform (Trichloromethane)	60	39	272	12	146/146	88	53	279	27	54/54
Carbon tetrachloride	280	220	2015	126	171/171	387	310	1475	131	66/66
HALOETHANES AND HALOPROPANES:										
Ethyl chloride	66	125	555	<10	19/19	47	28	107	21	11/11
1,2-Dichloroethane	--	--	--	--	--	--	--	--	--	--
1,2-Dibromoethane	21	49	436	<5	144/147	19	8	41	8	58/58
1,1,1-Trichloroethane	491	25	2679	164	172/172	403	257	1435	120	66/66
1,2-Dichloropropane	72	91	560	18	140/140	41	17	80	<10	54/54
CHLOROALKENES:										
Trichloroethylene	149	173	1003	12	166/166	164	188	921	12	63/63
Tetrachloroethylene	570	529	4337	76	284/284	792	901	4793	127	117/117
AROMATIC HYDROCARBONS:										
Benzene	1917	1721	11074	269	293/293	4367	6620	33960	117	99/99
Toluene	4260	4141	30576	382	287/297	7436	9340	44672	462	100/100
Ethyl benzene	760	778	7256	85	264/297	2678	4186	16648	<50	76/100
m/p-Xylene	1598	1489	14050	194	283/297	2635	3286	15594	<50	83/100
o-Xylene	847	847	5852	<50	232/297	2596	3549	17353	<50	56/100
3/4-Ethyl toluene	714	636	3891	<50	192/297	1603	1597	6644	<50	46/100
1,3,5-Trimethyl benzene	526	333	1374	<50	31/297	1565	1814	7286	<50	24/100
1,2,4-Trimethyl benzene	943	757	5363	<50	222/297	2858	4841	29696	<50	54/100
OXYGENATED SPECIES:										
Peroxyacetylnitrate (PAN)	1068	678	3721	<50	281/309	1578	1111	5475	386	116/116
Peroxypropionylnitrate (PPN)	139	94	501	<50	280/309	213	150	902	<50	116/118
Formaldehyde	--	--	--	--	--	--	--	--	--	--
Acetaldehyde	--	--	--	--	--	--	--	--	--	--

*Arithmetic Mean.

**One standard deviation.

†n is the number of positive (non-zero) measurements;
N is the total number of valid measurements.

TABLE 9. ATMOSPHERIC CONCENTRATIONS OF MEASURED CHEMICALS FOR DOWNEY, HOUSTON, AND DENVER

Chemical Group and Species	Downey 18-27 February 1984					Houston 9-17 March 1984				
	PPTV					PPTV				
	Mean*	S.D.**	Maximum	Minimum	n/N†	Mean	S.D.	Maximum	Minimum	n/N
CHLOROFLUOROCARBONS:										
Trichlorofluoromethane (F-11)	685	356	1718	168	45/47	488	142	1041	251	48/48
Dichlorodifluoromethane (F-12)	1183	779	3641	314	48/48	512	156	941	332	48/48
Trichlorotrifluoroethane (F-113)	118	53	313	48	47/47	58	16	114	36	48/48
Dichlorotetrafluoroethane (F-114)	34	20	89	12	47/47	18	3	30	12	47/47
HALOMETHANES:										
Methyl chloride	792	237	1655	470	48/48	961	361	2278	520	47/47
Methyl bromide	212	226	815	18	44/44	23	8	48	11	45/45
Methyl iodide	3	2	10	<1	45/45	12	10	51	2	47/47
Methylene chloride (Dichloromethane)	2399	1604	6641	443	47/47	324	300	1584	71	46/46
Chloroform (Trichloromethane)	135	81	385	26	64/64	249	243	1588	47	110/110
Carbon tetrachloride	199	71	331	103	48/48	291	175	1154	158	48/48
HALOETHANES AND HALOPROPANES:										
Ethyl chloride	28	17	106	11	43/43	448	871	2981	11	40/44
1,2-Dichloroethane	102	134	630	20	45/45	450	673	2456	<5	47/48
1,2-Dibromoethane	102	83	420	<5	52/61	293	550	3181	<5	104/106
1,1,1-Trichloroethane	1161	609	2727	161	64/64	375	208	1235	121	110/110
1,2-Dichloropropane	35	34	157	<2	43/64	158	108	724	<2	100/106
CHLOROALKENES:										
Trichloroethylene	184	155	738	22	64/64	61	106	880	<2	104/110
Tetrachloroethylene	1471	694	3711	341	64/64	169	245	1604	20	109/109
AROMATIC HYDROCARBONS:										
Benzene	8720	5940	28790	970	107/107	6130	5838	40320	1030	102/102
Toluene	16890	12251	63970	1640	106/106	7270	9479	78160	270	100/102
Ethyl benzene	4580	3712	16090	280	104/104	1540	1589	8200	<50	99/102
m/p-Xylene	10210	7785	37480	920	104/104	3340	3066	17910	<50	101/102
o-Xylene	4180	3219	15960	<50	103/103	1380	1389	7200	<50	89/102
3/4-Ethyl toluene	3220	2512	12270	<50	102/103	770	890	5920	<50	84/102
1,3,5-Trimethyl benzene	850	923	4040	<50	63/104	170	714	6760	<50	20/102
1,2,4-Trimethyl benzene	4020	3324	15590	<50	100/104	990	1005	7180	<50	76/102
OXYGENATED SPECIES:										
Peroxyacetylnitrate (PAN)	1231	1112	6671	67	207/207	751	787	7925	<50	188/193
Peroxypropionylnitrate (PPN)	60	67	403	<50	145/206	45	78	538	<50	89/189
Formaldehyde	15500	5900	41000	2000	48/48	3800	8300	22500	<400	11/11
Acetaldehyde	8500	6300	28400	1000	48/48	2200	1700	6700	<200	11/11

TABLE 9 (continued).

Chemical Group and Species	Denver 24 March - 1 April 1984 PPTV Mean*	S.D.**	Maximum	Minimum	n/N†
CHLOROFLUOROCARBONS:					
Trichlorofluoromethane (F-11)	555	89	770	412	42/42
Dichlorodifluoromethane (F-12)	648	546	2811	334	42/42
Trichlorotrifluoroethane (F-113)	41	41	282	22	42/42
Dichlorotetrafluoroethane (F-114)	26	8	64	17	41/41
HALOMETHANES:					
Methyl chloride	780	227	1602	573	41/41
Methyl bromide	22	11	64	13	41/41
Methyl iodide	2	1	8	1	42/42
Methylene chloride (Dichloromethane)	569	456	2699	104	42/42
Chloroform (Trichloromethane)	123	40	259	38	98/98
Carbon tetrachloride	264	26	363	225	42/42
HALOETHANES AND HALOPROPANES:					
Ethyl chloride	23	21	123	9	41/41
1,2-Dichloroethane	23	29	124	<5	31/38
1,2-Dibromoethane	122	84	601	<5	98/99
1,1,1-Trichloroethane	647	320	1850	256	98/98
1,2-Dichloropropane	163	62	312	<2	96/97
CHLOROALKENES:					
Trichloroethylene	53	49	241	5	99/99
Tetrachloroethylene	434	419	2499	51	99/99
AROMATIC HYDROCARBONS:					
Benzene	2230	2081	13480	380	85/85
Toluene	3340	3871	25780	390	85/85
Ethyl benzene	1100	3454	31480	<50	70/85
m/p-Xylene	1900	2322	14770	<50	82/85
o-Xylene	630	1142	6630	<50	50/85
3/4-Ethyl toluene	440	707	4220	<50	48/85
1,3,5-Trimethyl benzene	80	221	1300	<50	14/85
1,2,4-Trimethyl benzene	650	972	5650	<50	53/85
OXYGENATED SPECIES:					
Peroxyacetylnitrate (PAN)	644	348	2039	191	209/209
Peroxypropionylnitrate (PPN)	22	29	85	<50	82/209
Formaldehyde	2300	1800	5500	<400	21/21
Acetaldehyde	1000	500	2100	<200	21/21

*Arithmetic Mean.

**One standard deviation.

†n is the number of positive (non-zero) measurements;
N is the total number of valid measurements.

TABLE 10. ATMOSPHERIC CONCENTRATIONS OF MEASURED CHEMICALS FOR SAN JOSE

Chemical Group and Species	4-16 April 1985 PPTV					12-24 August 1985 PPTV				
	Mean*	S.D.**	Maximum	Minimum	n/N†	Mean	S.D.	Maximum	Minimum	n/N
CHLOROFLUOROCARBONS:										
Trichlorofluoromethane (F-11)	529	217	1613	252	119/119	450	179	1330	244	127/127
Dichlorodifluoromethane (F-12)	1020	477	2751	458	117/117	881	345	2058	427	129/129
Trichlorotrifluoroethane (F-113)	1256	755	4605	395	117/117	616	407	2410	166	126/126
Dichlorotetrafluoroethane (F-114)	59	39	239	19	115/115	72	143	888	12	123/123
HALOMETHANES:										
Methyl chloride	1060	274	2508	673	116/116	--	--	--	--	--
Methyl bromide	400	549	4661	44	114/114	121	146	1067	<5	112/114
Methyl iodide	5	6	51	1	104/104	3	2	<10	1	128/128
Methylene chloride (Dichloromethane)	1534	906	4311	403	117/117	1119	1056	8257	142	128/128
Chloroform (Trichloromethane)	64	27	138	23	119/119	58	35	180	11	139/139
Carbon tetrachloride	193	51	398	55	119/119	144	20	213	85	142/142
HALOETHANES AND HALOPROPANES:										
Ethyl chloride	--	--	--	--	--	--	--	--	--	--
1,2-Dichloroethane	--	--	--	--	--	--	--	--	--	--
1,2-Dibromoethane	21	7	41	9	40/40	--	--	--	--	--
1,1,1-Trichloroethane	360	174	905	120	118/118	283	68	518	133	142/142
1,2-Dichloropropane	31	14	70	9	87/87	25	9	61	9	136/136
CHLOROALKENES:										
Trichloroethylene	63	48	266	8	113/113	68	54	266	10	141/141
Tetrachloroethylene	427	259	1530	58	115/115	264	169	767	36	139/139
AROMATIC HYDROCARBONS:										
Benzene	3296	2239	11747	379	123/123	2060	1258	7816	441	145/145
Toluene	5667	4206	22155	637	122/122	3904	2742	19612	709	145/145
Ethyl benzene	1213	1108	6355	131	122/122	859	736	4088	173	144/144
m/p-Xylene	3619	2701	14641	649	122/122	1981	1431	8380	515	140/140
o-Xylene	1361	950	5085	121	119/119	913	659	5125	216	141/141
3/4-Ethyl toluene	1023	756	4066	128	120/120	649	433	2927	147	142/142
1,3,5-Trimethyl benzene	224	208	1608	69	121/121	168	124	773	34	141/141
1,2,4-Trimethyl benzene	1272	832	4518	233	116/116	715	521	3591	112	135/135
OXYGENATED SPECIES:										
Peroxyacetylnitrate (PAN)	--	--	--	--	--	--	--	--	--	--
Peroxypropionylnitrate (PPN)	--	--	--	--	--	--	--	--	--	--
Formaldehyde	--	--	--	--	--	--	--	--	--	--
Acetaldehyde	--	--	--	--	--	--	--	--	--	--

TABLE 10. (CONTINUED)

Chemical Group and Species	13-21 December 1985				
	PPTV				
	Mean*	S.D.**	Maximum	Minimum	n/N†
CHLOROFLUOROCARBONS:					
Trichlorofluoromethane (F-11)	585	170	971	239	80/80
Dichlorodifluoromethane (F-12)	1435	376	2450	670	91/91
Trichlorotrifluoroethane (F-113)	1211	351	2321	476	92/92
Dichlorotetrafluoroethane (F-114)	227	245	967	34	94/94
HALOMETHANES:					
Methyl chloride	1118	581	4870	194	92/92
Methyl bromide	2869	3098	15424	239	92/92
Methyl iodide	9	4	23	3	80/80
Methylene chloride (Dichloromethane)	4181	1795	10310	1034	91/91
Chloroform (Trichloromethane)	102	38	203	38	93/93
Carbon tetrachloride	155	43	266	90	93/93
HALOETHANES AND HALOPROPANES:					
Ethyl chloride	--	--	--	--	--
1,2-Dichloroethane	--	--	--	--	--
1,2-Dibromoethane	7	3	18	2	61/61
1,1,1-Trichloroethane	1219	721	3174	345	93/93
1,2-Dichloropropane	24	5	35	9	85/85
CHLOROALKENES:					
Trichloroethylene	271	194	907	71	93/93
Tetrachloroethylene	1858	1202	6639	311	93/93
AROMATIC HYDROCARBONS:					
Benzene	12372	4501	23425	3921	95/95
Toluene	21155	8801	45947	6676	95/95
Ethyl benzene	6176	3046	14453	1553	95/95
m/p-Xylene	13144	5809	25330	3672	95/95
o-Xylene	5714	2170	11001	2024	95/95
3/4-Ethyl toluene	4224	1574	8285	1476	95/95
1,3,5-Trimethyl benzene	1298	575	2662	254	95/95
1,2,4-Trimethyl benzene	5367	1903	10376	1838	95/95
OXYGENATED SPECIES:					
Peroxyacetylnitrate (PAN)	--	--	--	--	--
Peroxypropionylnitrate (PPN)	--	--	--	--	--
Formaldehyde	--	--	--	--	--
Acetaldehyde	--	--	--	--	--

*Arithmetic Mean.

**One standard deviation.

†n is the number of positive (non-zero) measurements;
N is the total number of valid measurements.

bars. In San Jose, 2-hour integrated samples were collected. The diurnal patterns for San Jose were calculated identically to the other cities, except that 2-hour intervals (midnight to 2 a.m., 2 a.m. to 4 a.m., etc.) were used.

Because many of the chemicals measured here are also ubiquitous components of the global troposphere, Table 11 has been prepared to define this background at midlatitudes in the Northern Hemisphere. The concentrations are estimated for the year 1985 and are derived from published values and our measurements at Point Arena, California (Singh et al, 1983b-e, 1986; Prinn et al, 1983; Simmond et al, 1983; Singh, 1984).

Interpretation of field data is greatly facilitated when some knowledge of the chemical loss rate exists. In a given day, the diurnal behavior of chemicals is controlled both by the mixing process as well as chemical loss. It is well known that the hydroxyl radical (HO) plays a central role in depleting atmospheric organics, both in the polluted and the clean atmospheres. For the halogenated (except methyl iodide) and aromatic hydrocarbons of interest here, we have concluded that no significant error in loss rates is incurred when reactions with species other than HO, such as $O(^3P)$, O_3, HO_2, are neglected. In the case of the aldehydes and of methyl iodide, both reaction with HO and photolysis are important.

The residence times of PAN and PPN are largely controlled by their thermal decomposition, and are estimated from mechanisms suggested by Hendry and Kenley (1979). For the purposes of these calculations, an average daytime HO radical abundance of 2×10^6 molecule/cm^3 is assumed. These HO levels are well supported by HO estimates from available field data (Calvert, 1976; Singh et al, 1981a; Roberts et al, 1984), and are probably typical of the boundary layer of polluted urban environments in summer months. The only wintertime estimate available is from Southern California (Singh et al, 1985b) and suggests, at least at this site, that OH levels are comparable to their summer values. The kinetic and photolytic data utilized in Table 12 are taken from Atkinson et al (1979), Hampson (1980), Hudson and Reed (1980), and estimated from Hendry and Kenley (1979), and Hendry et al (1980).

Table 12 provides these data, and estimates the percentage loss due to chemical reaction in one day (12 sunlit hours). For virtually all species of

TABLE 11. ESTIMATED AVERAGE BACKGROUND CONCENTRATION OF TRACE SPECIES AT 40°N FOR YEAR 1985

Chemical Group and Species	Concentration (ppt)
CHLOROFLUOROCARBONS:	
Trichlorofluoromethane (F-11)	240
Dichlorodifluoromethane (F-12)	300
Trichlorotrifluoroethane (F-113)	35
Dichlorotetrafluoroethane (F-114)	16
HALOMETHANES:	
Methyl chloride	650
Methyl bromide	15-30
Methyl iodide	2
Methylene chloride (Dichloromethane)	50
Chloroform (Trichloromethane)	20
Carbon tetrachloride	140
HALOETHANES AND HALOPROPANES:	
Ethyl chloride	10
1,1 Dichloroethane	-*
1,2-Dichloroethane	40
1,2-Dibromoethane	2
1,1,1-Trichloroethane	200
1,2-Dichloropropane	-
CHLOROALKENES:	
Trichloroethylene	15
Tetrachloroethylene	50
AROMATIC HYDROCARBONS:	
Benzene	230
Toluene	130
Ethyl benzene	-
m/p-Xylene	30
o-Xylene	10
3/4-Ethyl toluene	-
1,3,5-Trimethyl benzene	-
1,2,4-Trimethyl benzene	-
OXYGENATED SPECIES:	
Peroxyacetylnitrate (PAN)	50
Peroxypropionylnitrate (PPN)	3
Formaldehyde	400
Acetaldehyde	200

*Dashes indicate absence of available data.

TABLE 12. ESTIMATED DAILY LOSS RATES (%) OF SELECTED TRACE CHEMICALS

Chemical Name	Dominant Removal Mechanism (reaction with)	Rate Constant at 300K* ($k \times 10^{12}$)	Percentage Loss in One Day (12 sunlit hours)†
Methyl chloride	HO	0.05	0.4
Methyl bromide	HO	0.04	0.4
Methyl iodide	photolysis	$\simeq 3 \times 10^{6}$‡	12.2
Methylene chloride	HO	0.15	1.3
Chloroform	HO	0.10	0.9
Carbon tetrachloride	Strat. photolysis	<0.0001	$\simeq$ 0.0
Ethyl chloride	HO	0.39	3.3
1,1 Dichloroethane	HO	0.26	2.3
1,2 Dichloroethane	HO	0.22	1.9
1,2 Dibromoethane	HO	0.25	2.2
1,1,1 Trichloroethane	HO	0.01	<0.1
1,1,2 Trichloroethane	HO	0.33	2.8
Tetrachloroethane (isom)	HO	<0.01	<0.1
1,2 Dichloropropane	HO	1.3§	10.2
Vinylidene chloride	HO	4.0§	29.2
(cis) 1,2 Dichloroethylene	HO	4.0	29.2
Trichloroethylene	HO	2.2	17.2
Tetrachloroethylene	HO	0.17	1.5
Allyl chloride	HO	28§	91.1
Hexachloro-1,3 butadiene	HO (?)	–	–
Chlorobenzene	HO	0.9§	7.4
α-chlorotoluene	HO	3.0§	22.8
Dichlorobenzene (o,m,p)	HO	0.3§	2.6
Trichlorobenzene (isom)	HO	0.1§	0.9
Benzene	HO	1.4	11.4
Toluene	HO	6.0	40.9
Ethyl benzene	HO	8.0	51.0
m-Xylene	HO	23.4	86.5
p-Xylene	HO	12.3	67.0
o-Xylene	HO	13.9	71.3
4-Ethyl toluene	HO	12.9	67.0
1,2,4 Trimethyl benzene	HO	33.2	96.4
1,3,5 Trimethyl benzene	HO	49.2	99.3
Formaldehyde	HO, photolysis	11.0, 2.8×10^{7}‡	88.2
Acetaldehyde	HO, photolysis	15.0, 1.4×10^{7}‡	85.1
Phosgene	–	–	–
Peroxyacetyl nitrate (PAN)	Thermal	–	99.9**
Peroxypropionyl nitrate (PPN)	Thermal	–	99.9**

*Rate constant with hydroxyl radical (HO) in units of $cm^3 molec^{-1} s^{-1}$.

†Calculated based on an estimated daytime (12 hour) average HO abundance of 2×10^6 molec/cm^3.

‡Rate constant due to photolysis in units of s^{-1}.

§Estimated from Hendry and Kenley (1979).

**Thermal degradation in the presence of NO and NO_2.

Table 12, nighttime loss rates are negligibly small. This percentage loss is defined as:

$$\text{percent loss} = [1 - \exp(-4.32 \times 10^{4}K)] \times 100,$$

where $K = k_{HO}(HO) + k_{h\nu} + k_{thermal}$.

It is clear from Table 12 that daily chemical loss rates ranging from near-zero to 100 percent per day, consistently occur in the atmosphere. Chloromethanes and chloroethanes, collectively a dominant group, are relatively unreactive, and a daily loss rate of 0 to 3 percent per day is estimated. In the entire haloalkane group, methyl iodide is the only species that is relatively rapidly removed by photolytic decomposition (~12 percent/day loss rate). The daily loss rate of aromatic hydrocarbons, aldehydes, and PAN is quite substantial.

In most cases listed in Table 12, the loss rate should be somewhat lower in winter months because of reduced temperatures and solar flux. In the case of PAN the effect of temperature is extremely dominant, and could very substantially reduce its loss rate (Hendry and Kenley, 1977; Cox and Roffey, 1977).

INTERPRETATION OF FIELD DATA BY CHEMICAL CATEGORY

Chlorofluorocarbons (CFCs)

Four fluorocarbons (Fluorocarbons 11, 12, 113, and 114) were routinely measured. These chemicals are not considered or expected to be toxic but can be useful indicators of urban air masses. Their involvement in stratospheric ozone destruction is well known (Molina and Rowland, 1974). It is clear from Tables 8-10 tht F12 is the most dominant species, both in urban and remote atmospheres. The F12/F11 ratio in urban centers varied from 1.1 to 2.4 and had a mean value of 1.7. This compares favorably with a ratio of 1.6 found in the free troposphere (Table 11). It is noted that background concentrations of these fluorocarbons have been increasing at a rate of 5 to 7 percent per year (Singh et al., 1983b). F113 is a commonly used solvent in the electronics industry. It is interesting to note that its concentration in the

San Jose field studies was far in excess of what is encountered in other locations. Figure 8 shows the mean diurnal behavior of F113 as measured at the San Jose site during April, August, and December of 1985 (see section 5 for the exact computational procedure used to obtaining these diurnal profiles). Indeed the abundance of F113 was comparable to that of F12 in San Jose during all seasons, while it was nearly an order of magnitude lower at virtually all other sites including the remote troposphere. A maximum mixing ratio for F113 of 4.6 ppb was measured at San Jose (Table 10) compared to a maximum F12 value of 3.6 ppb measured at the Downey Site (Table 8) in Southern California. Very little urban data on the distribution of fluorocarbons are available. Comparison of average concentrations with those earlier reported by Singh et al (1983e) and Brodzinsky and Singh (1983) suggest that the relative abundance is showing a pattern, with F113 exhibiting the most relative change in its abundance. Typical average concentrations at these site are 1.5 to 5 times the global background concentrations (Table 11). In the case of F113, however, this ratio was as high as 35 in San Jose (Table 10). Figures 9 and 10 show the diurnal behavior of fluorocarbon 12 and 114 at selected sites and in different seasons. The highest F12 values in San Jose were encountered during the winter experiment [Figure 10(c)], a period of high stagnation.

Halomethanes

Six halomethanes--methyl chloride, methyl bromide, methyl iodide, methylene chloride, chloroform, and carbon tetrachloride--were measured. All six of these are bacterial mutagens or suspected carcinogens (Singh et al, 1982; Helmes, et al, 1983). Three methyl halides have dominant natural (oceanic) sources (Lovelock, 1975; Singh et al, 1983b,c; Singh, 1984).

Methyl Chloride--

The dominant natural halocarbon in the atmosphere is methyl chloride. A nearly uniform background concentration of 0.6 to 0.7 ppb has been measured around the globe (Table 11), and no temporal trend in its background concentration is evident (Singh et al, 1979b; 1983c). Urban levels of methyl chloride have not been frequently reported in the literature, although Watson

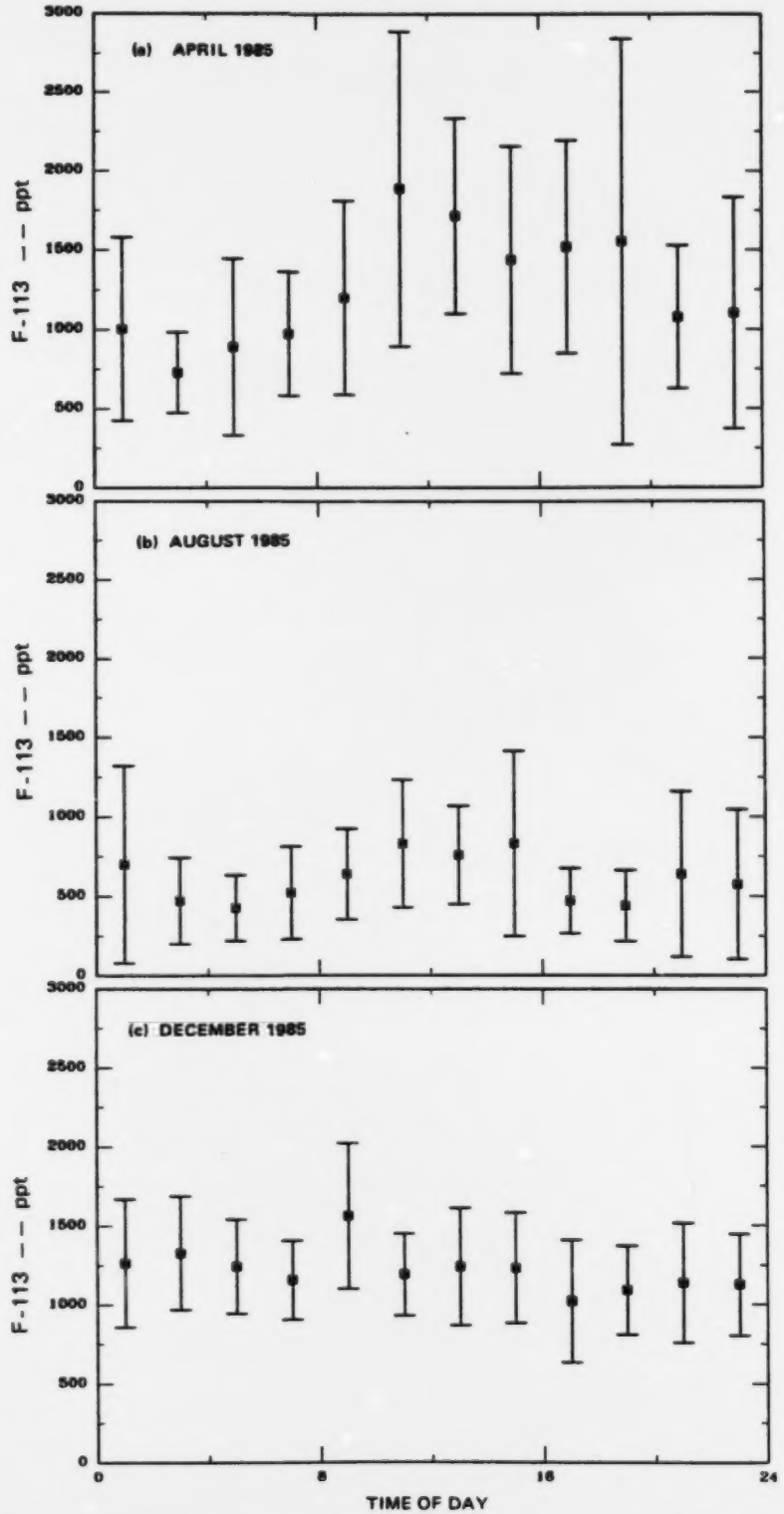

Figure 8. Diurnal behavior of fluorocarbon-113 at the San Jose site during April, August and December, 1985.

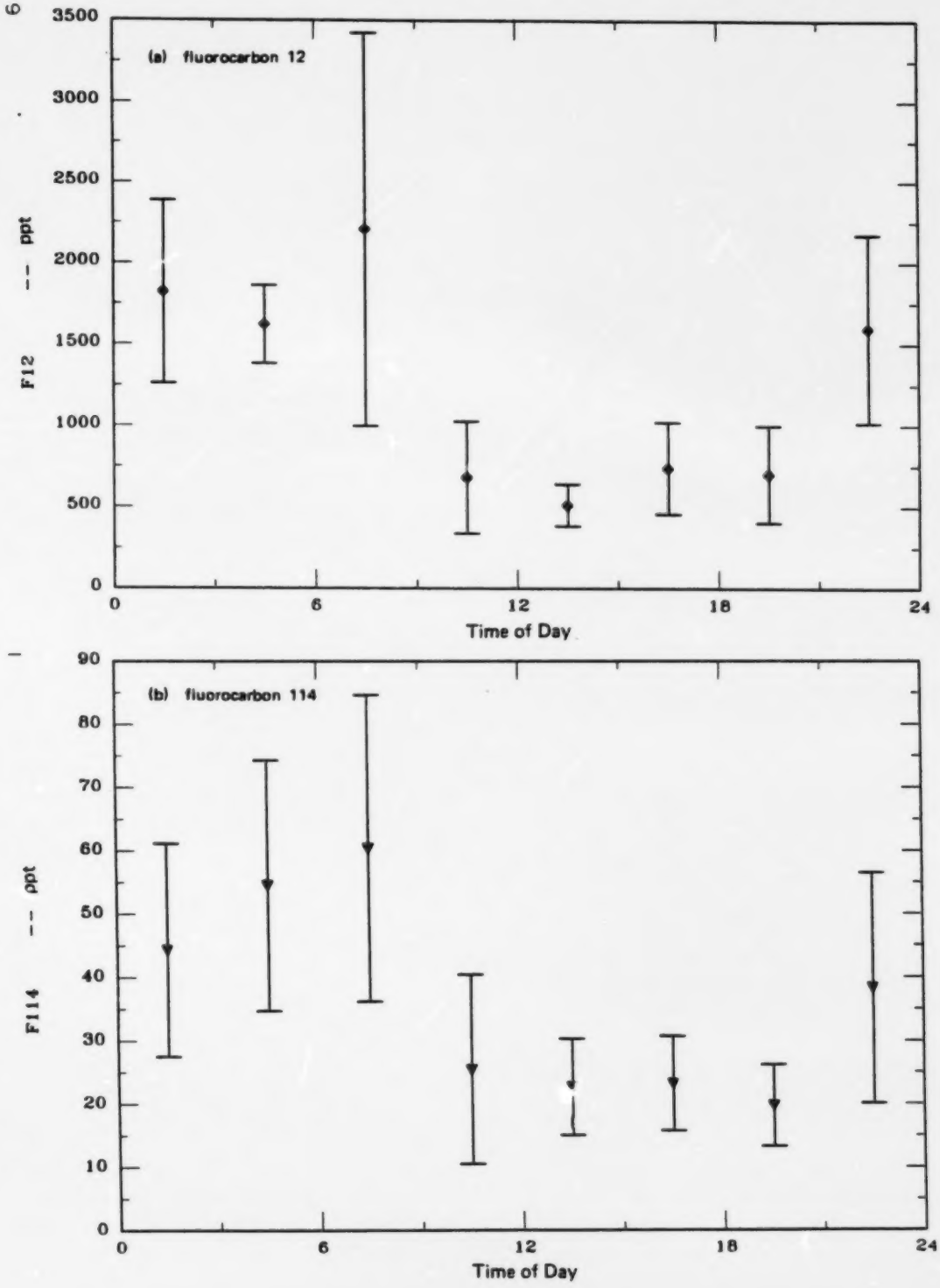

Figure 9. Diurnal behavior of fluorocarbons 12 and 114 at Downey, CA site.

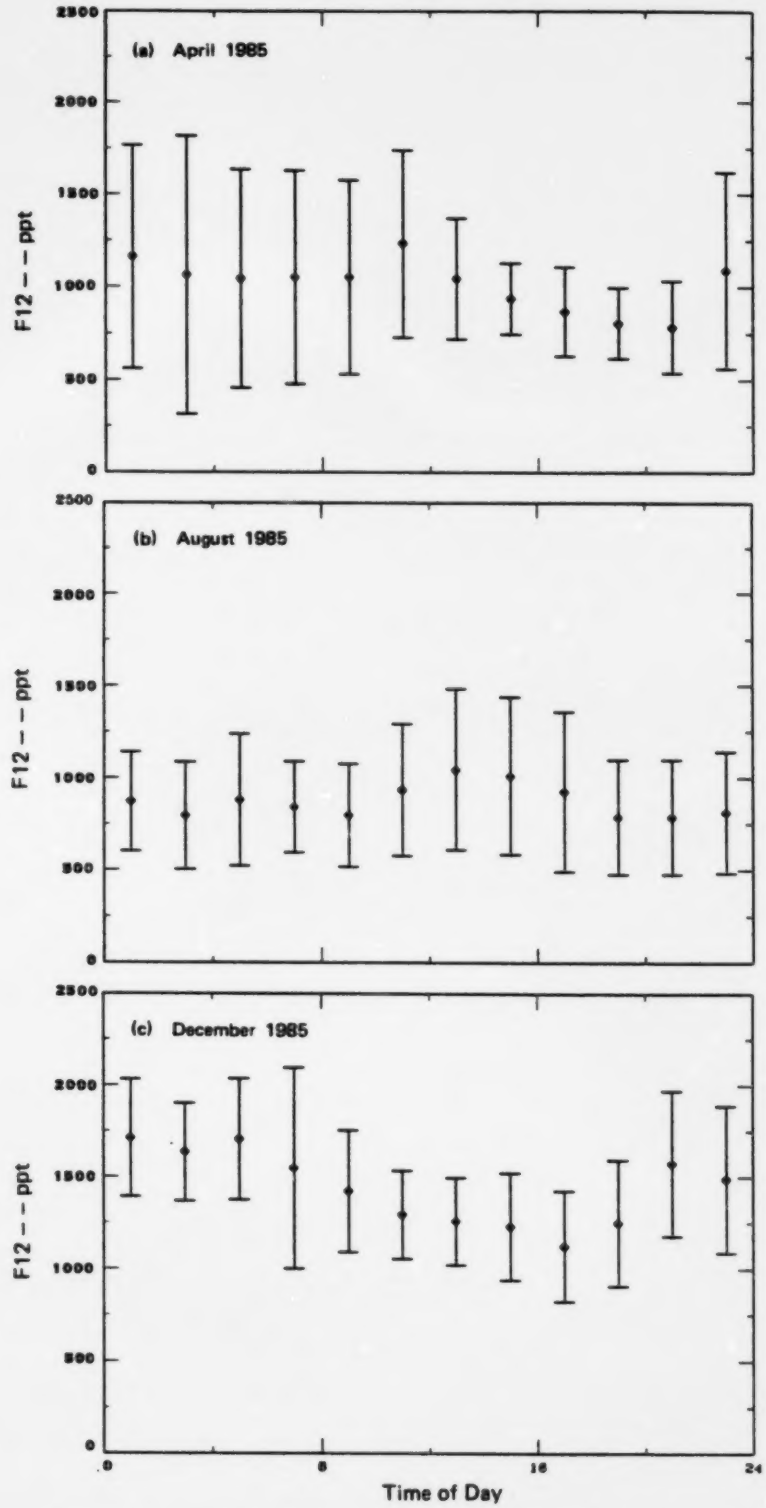

Figure 10. Diurnal behavior of fluorocarbon 12 at San Jose site during April, August, and December 1985.

et al, (1979) did report methyl chloride levels of over 2 ppb in Kenya. Based on our measurements (Tables 8 through 10), it appears that although typical methyl chloride levels in urban areas are close to, or only slightly elevated above, background levels, concentrations about five times higher than the background may be encountered. The average methyl chloride levels of 0.60 to 1.1 ppb measured here are only slightly elevated above the geochemical background. The direct man-made sources of methyl chloride are negligibly small compared to the oceanic source of nearly 3 Tg/year. Nevertheless anthropogenic sources, possibly related to combustion activity, are clearly present in urban centers. Figure 11 shows the concentrations of methyl chloride and its mean diurnal behavior at the Denver and Houston sites. In both instances there is evidence of anthropogenic influences, but the effect is much larger in Houston compared to Denver. Methyl chloride is slowly decomposed in the atmosphere (daily loss rate <0.5 percent), and its global residence time is estimated to be between 1 and 2 years (Singh et al, 1983c; Table 10).

Methyl Bromide--

Average methyl bromide concentrations of 0.02 to 0.3 ppb were measured during the first five studies. In San Jose, mean concentrations of 0.4 ppb, 0.1 ppb, and 2.9 ppb were measured in April, August, and December, respectively. A maximum concentration of 15.4 ppb was also measured during the winter experiment. These very high values are contrary to our previous measurements at other sites. The possibility that this site is impacted by unknown local sources of methyl bromide cannot be ruled out. A background concentration of 15-20 ppt is known to be present, with oceans as the major source. Methyl bromide is used as an agricultural fumigant and its concentrations in urban areas are clearly elevated. It has been suggested that the gasoline additive 1,2-dibromomethane could breakdown to produce methyl bromide (NAS, 1978). This additive is normally used in leaded gasoline and may be a source in urban areas. Although measurements of methyl bromide in the marine atmospheres are extensive (Singh et al, 1983c; Singh et al, 1984; Berg et al, 1984; Penkett et al, 1985) virtually no data are available from urban locations. The present measurements (except at San Jose) are similar to our

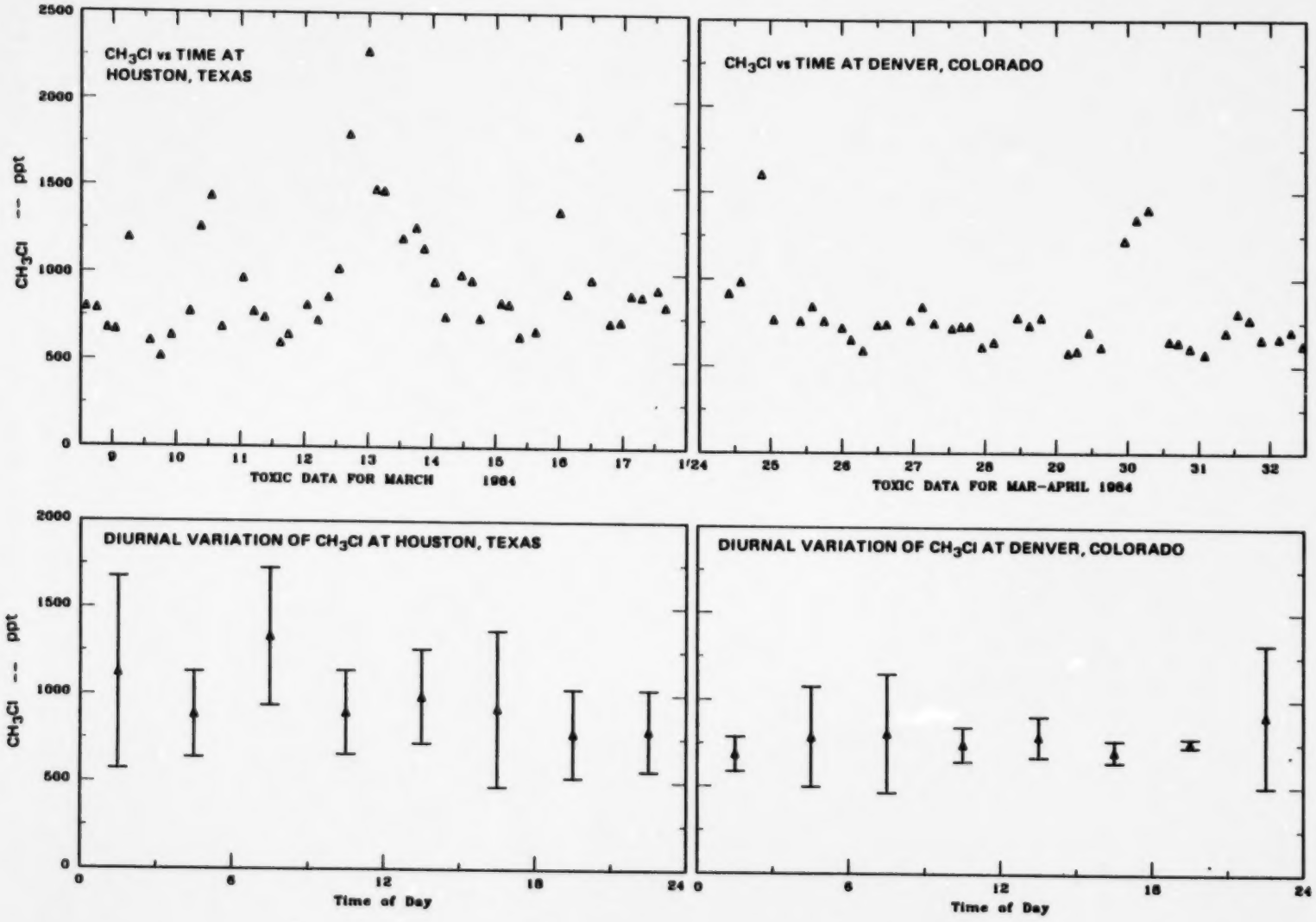
CH3Cl vs TIME AT HOUSTON, TEXAS
CH3Cl vs TIME AT DENVER, COLORADO
CH3Cl -- ppt
TOXIC DATA FOR MARCH 1984
TOXIC DATA FOR MAR-APRIL 1984
DIURNAL VARIATION OF CH3Cl AT HOUSTON, TEXAS
DIURNAL VARIATION OF CH3Cl AT DENVER, COLORADO
Time of Day

Figure 11. Methyl chloride distribution and diurnal behavior at the Houston and Denver sites.

earlier ones where we reported typical methyl bromide concentrations of less than 0.1 ppb with highest values in the 1 ppb range (Singh et al, 1982; 1983e). At Staten Island, mean concentrations of 84 ppt and 80 ppt were measured in 1981 (Singh et al, 1983e) and 1983 (Table 8) respectively. In both Houston and Denver, the measured concentrations were nearly fourfold lower compared to the previously measured spring/summer values. This is primarily due to the unstable weather conditions that prevailed during these experiments. The San Jose concentrations are among the highest measured to date. It is evident that significant methyl bromide sources in urban areas exist. Their nature and strength, however, is not known. Figure 12 shows the variability of methyl bromide and its diurnal behavior at the Downey, CA site. Methyl bromide is chemically removed from the atmosphere at a rate similar to that of methyl chloride (Table 12). There is some speculation that methyl bromide levels may increase over the years, causing it to be a major depletor of stratospheric ozone (Penkett et al, 1985). This view, however, assumes that most of atmospheric methyl bromide comes from man-made sources rather than the oceans. Sea water measurements performed to date (Singh et al 1983c) show supersaturated oceans that contain 1.2 ng/ℓ of methyl bromide. It is further found that both methyl chloride and methyl bromide probably have a common source in the oceans.

Methyl Iodide--

Methyl iodide, along with the other methyl halides, finds a large source in the oceans and is known to be mutagenic (Helmes et al, 1983). Unlike the other methyl halides, the iodide is decomposed rapidly by sunlight. A daily loss rate of about 12 percent is estimated (Table 11). Oceans have been found to be super-saturated with methyl iodide, with a typical surface concentration of 1 ng/ℓ over the eastern Pacific. This supersaturation is much higher in the shallow coastal zones. A surface background concentration of 2-5 ppt is known to exist (Singh et al, 1983c). Except during experiments at Houston and San Jose (winter), methyl iodide concentrations are indistinguishable from its natural background. We do not expect it to have any significant man-made sources. However, concentrations well above the natural background were measured. The Houston experiment was performed during periods of heavy rain

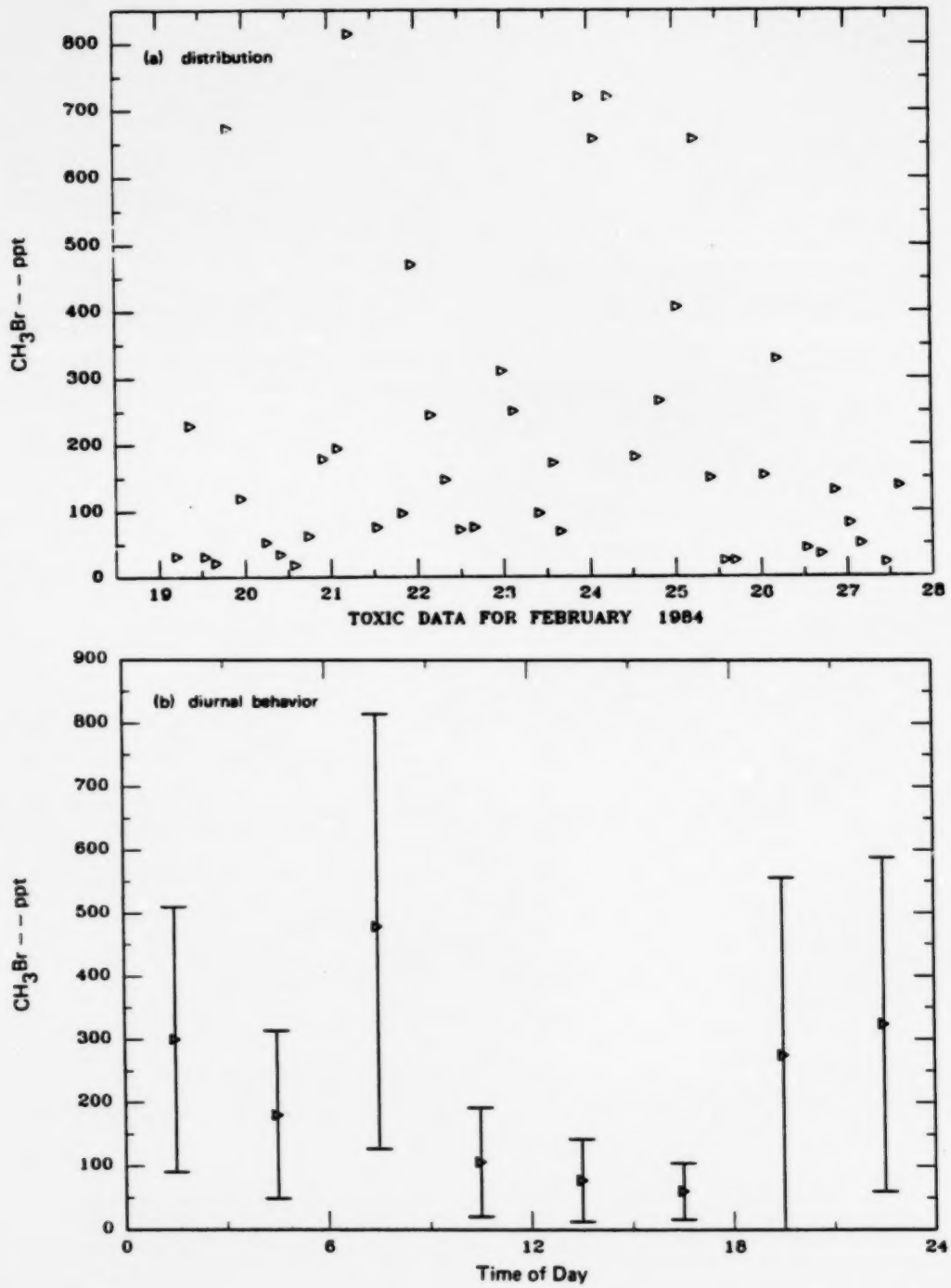

Figure 12. Methyl bromide distribution and its diurnal behavior at Downey, CA site.

while the winter San Jose experiment was performed under stagnant conditions. The possibility of localized sources or unknown interferences cannot be ruled out. The global budgets of methyl halides have been reviewed by Singh (1984). Figure 13 shows the diurnal behavior of methyl iodide at the Downey site.

Methylene Chloride--

Methylene chloride is a large volume chemical (Table 7) of anthropogenic origin and is a commonly used solvent. To the best of our knowledge, no natural sources are known to exist. World-wide man-made emissions are estimated to be 0.4 Tg/yr. The global distribution of methylene chloride in the background atmosphere shows Northern Hemispheric (NH) concentrations to be about twice the Southern Hemispheric (SH) values (Singh et al, 1983b). At 40°N its background concentration is about 50 ppt. Average methylene chloride concentrations at all sites were in the ranges of 0.3 ppb to 4.1 ppb. The highest average was measured during the winter experiment in San Jose which coincided with highly stagnant meteorological conditions. A maximum concentration of 10.3 ppb was also measured during this time (Table 10). As has been typical of our previous studies in Southern California, the measured levels at the Downey site were also quite high. This average concentration of 2.4 ppb can be compared to an earlier value of 3.8 ppb measured in Los Angeles in 1979 (Singh et al, 1983e). In virtually all cases the average concentrations of methylene chloride were an order of magnitude higher than its geochemical background. Methylene chloride is relatively unreactive, and a daily loss rate of 2 percent is estimated. Figure 14 shows the diurnal behavior of methylene chloride at the San Jose site during April, August, and December. As stated earlier the elevated levels during the December experiment are principally attributable to stagnation. Its diurnal behavior at the Philadelphia and Downey sites is also similar to that observed in San Jose for the same season (Figure 15).

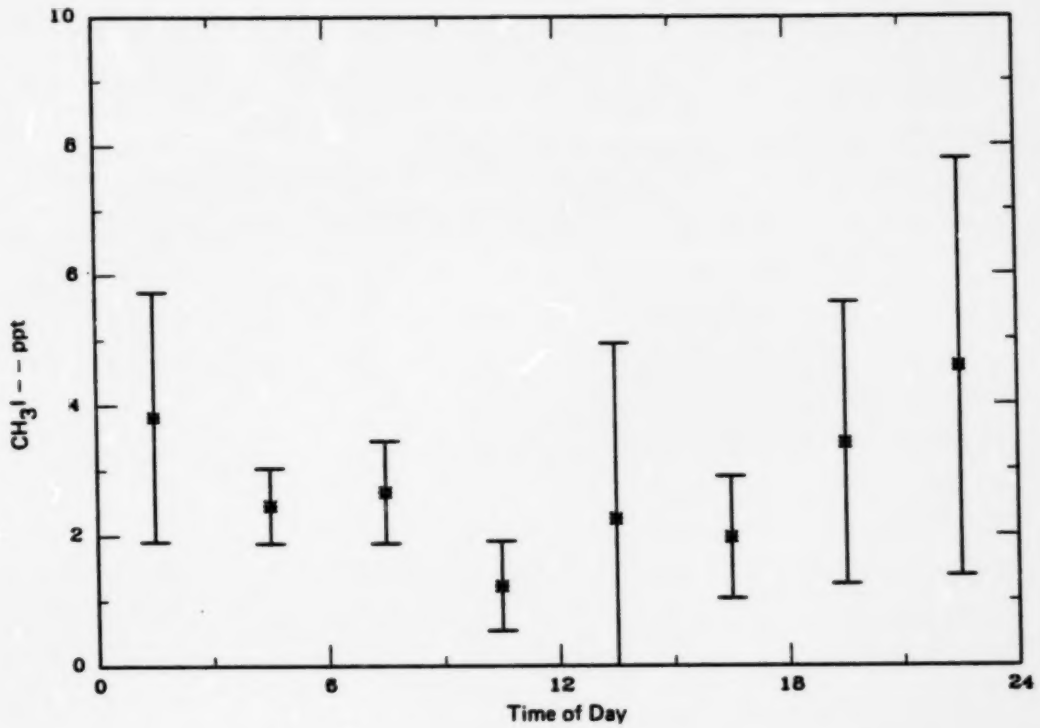

Figure 13. Diurnal behavior of methyl iodide at Downey, CA site.

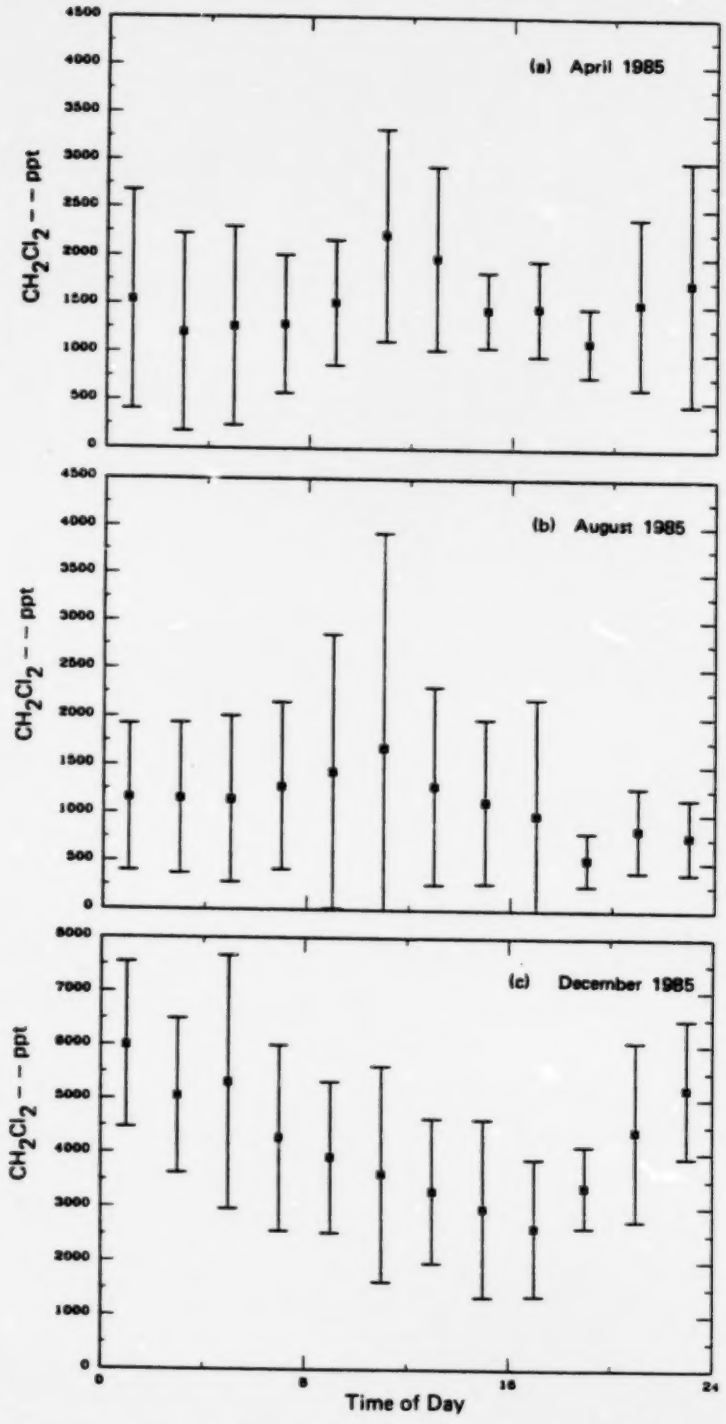

Figure 14. Diurnal behavior of methylene chloride at San Jose site during April, August, and December 1985.

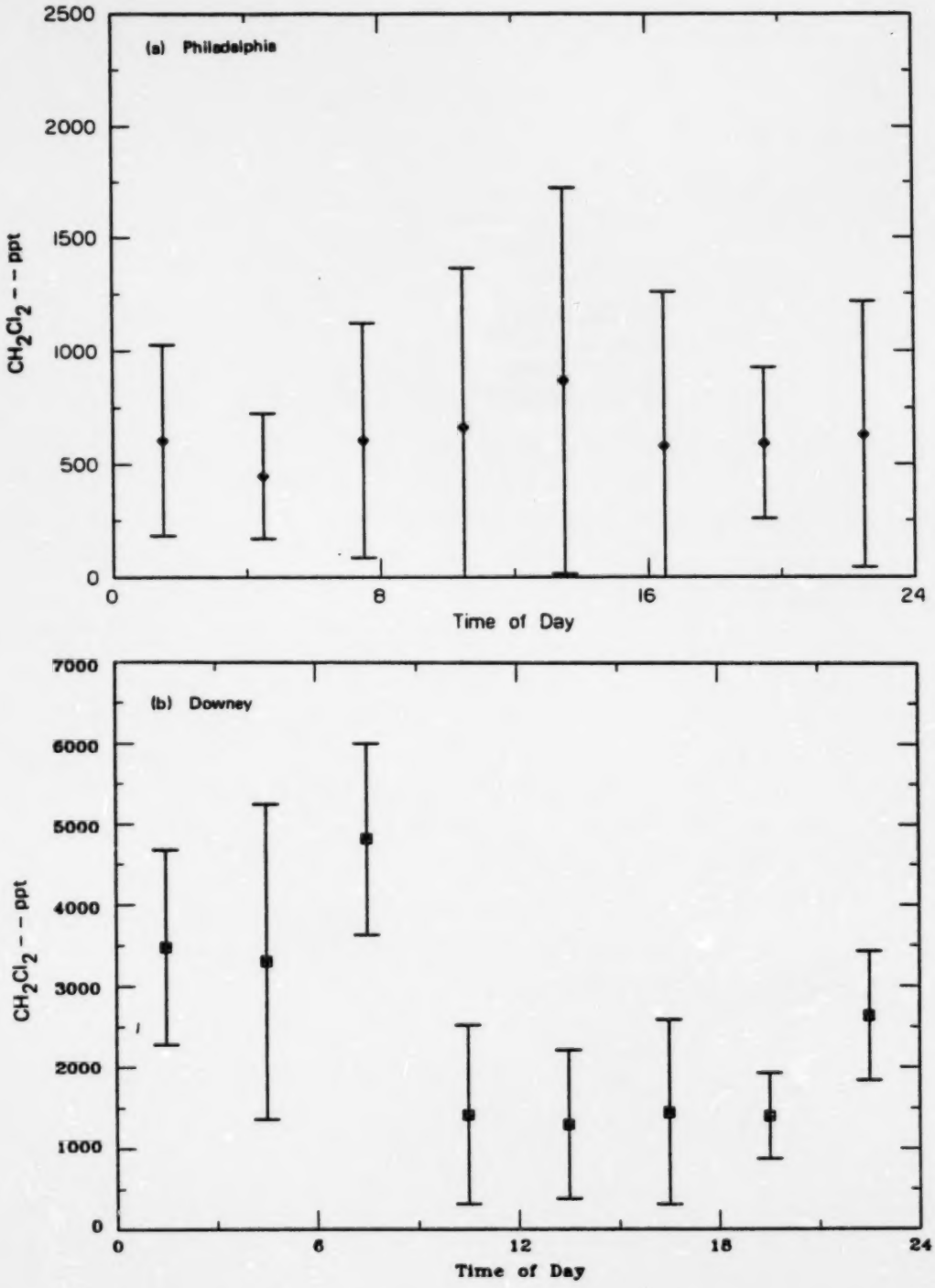

Figure 15. Diurnal behavior of methylene chloride at Philadelphia and Downey (CA) sites.

Chloroform--

Chloroform, a mutagen and a suspect carcinogen (Helmes, et al, 1983) has received a great deal of attention in recent years because of its high concentrations in drinking water (Symons et al, 1975). Its NH background concentration is in the 20 to 30 ppt range with a NH/SH gradient of 1.5 to 2. The U.S. production rate has remained more or less constant at 0.15 to 0.2 Tg/yr with nearly 90 percent of the production going towards the manufacture of fluorocarbon 22. It is estimated that world-wide emissions are about 0.02 Tg/year (Singh, 1984) while the atmospheric reservoir requires a source of 0.5 Tg/yr. Clearly then, a majority of chloroform sources are not industrial and are probably ill defined (Batjer et al, 1980). There is tentative evidence that oceans may be the largest single source of chloroform (Singh, 1984). Tables 8 through 10 show that in urban areas chloroform concentrations are well above its geochemical background. Average concentrations in the range of 0.06 to 0.25 ppb and maximum concentrations in the range of 0.2 to 1.6 ppb were measured. In our previous studies, we have encountered concentrations as high as 5 ppb (Singh et al, 1983e). The reactivity of chloroform is comparable to methylene chloride, and its diurnal behavior is principally controlled by meteorological processes. Once again, the urban as well as the global sources of chloroform are not well defined. Figure 16 shows the diurnal behavior of chloroform at the San Jose site during April, August, and December. Chloroform concentrations in Downey (Figure 17) are higher than San Jose even when the latter encountered highly stagnant meteorological conditions in December.

Carbon Tetrachloride--

Carbon tetrachloride, a suspect carcinogen, is nearly uniformly distributed in the global atmosphere at a sizable background concentration of about 140 ppt (Helmes et al, 1983; Singh, 1984). Although large natural sources of carbon tetrachloride have been speculated, none have been found. Best analysis of available data (Singh et al, 1976; Altshuller et al, 1976; Simmond et al, 1983) would suggest that it is principally a man-made chemical. The average geochemical background concentrations of 0.14 ppb can be compared with an average concentration of 0.14 to 0.4 ppb measured during these studies

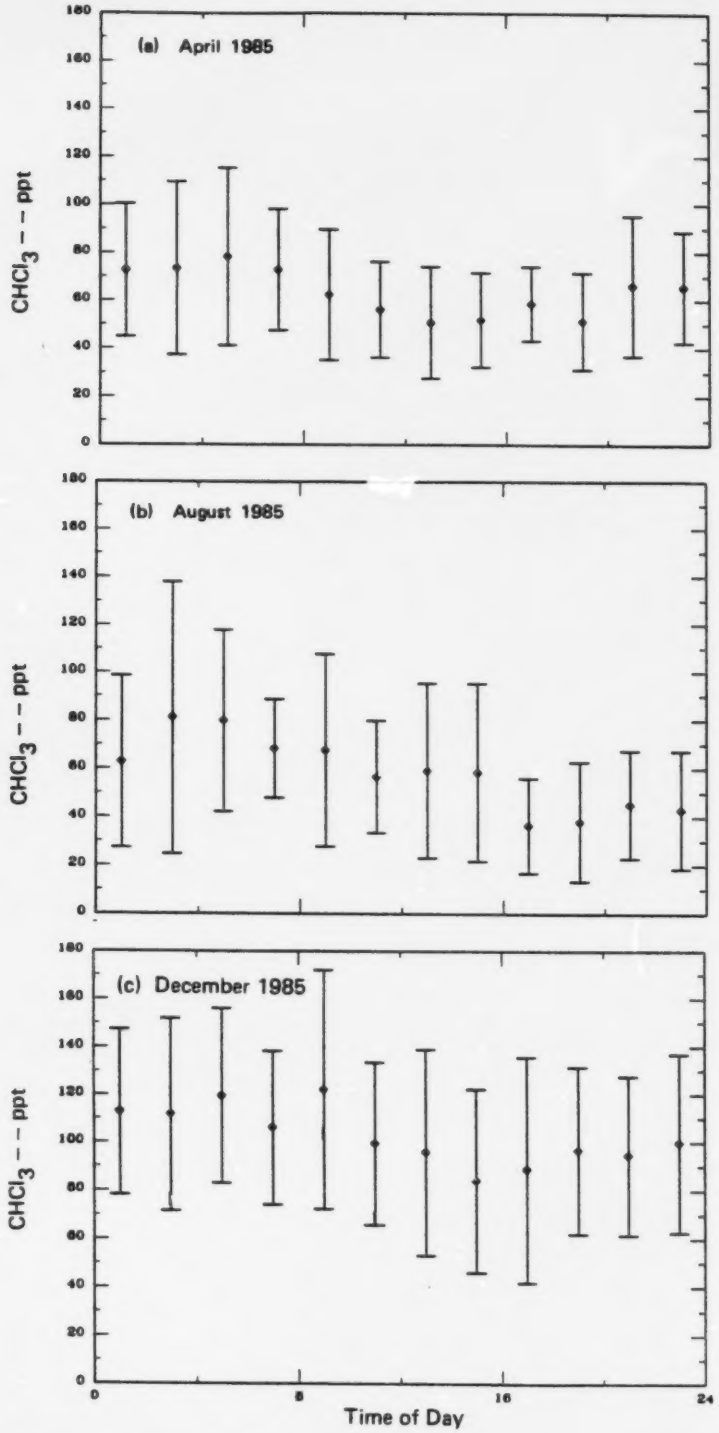

Figure 16. Diurnal behavior of chloroform at San Jose site during April, August, and December 1985.

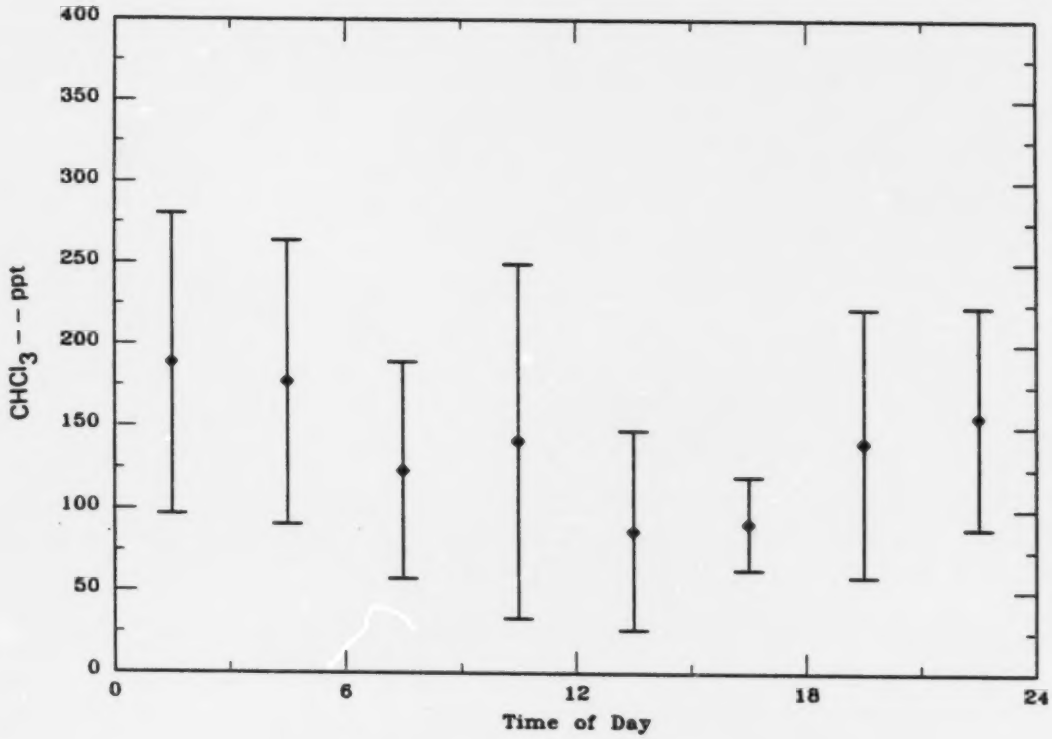

Figure 17. Diurnal behavior of chloroform at the Downey site.

(Tables 8 through 10). Sporadic concentrations as high as 2 ppb were also encountered (Table 8). A maximum concentration of 1.2 ppb measured at the Houston Site in March 1984 can be compared to a maximum 3 ppb concentration measured in May 1980 at this same site (Singh et al, 1983e). Figure 18 shows the diurnal behavior of carbon tetrachloride as measured at the Downey and San Jose (winter) sites.

Haloethanes and Halopropanes

Five important chemicals in this category were measured. Four of these (including ethyl chloride) are either bacterial mutagens or suspect carcinogens (Helmes et al, 1983; Singh et al, 1982).

Ethyl Chloride--

Ethyl chloride is a commonly used chemical intermediate (Table 7). It is estimated that about 0.01 million tons of ethyl chloride are released into the atmosphere every year in the United States. A daily chemical loss rate of about 3 percent is estimated (Table 12). Average ethyl chloride concentrations at all sites were in the 0.02 to 0.07 ppb range, except at the Houston site where they were significantly higher. The average concentration at Houston (Table 9) was 0.45 ppb and a maximum concentration of 3.0 ppb was also encountered here. This is consistent with our previous measurements (Singh et al, 1983e) at this site where average and maximum levels of 0.23 ppb and 1.3 ppb, respectively, were measured. The average of all urban data are reported to be less than 0.1 ppb by Brodzinky and Singh, (1983). Background concentration of ethyl chloride (at 40°N) is found to lie between 10 to 15 ppt (Table 11), clearly suggesting that significant urban sources exist.

Ethylene Dichloride (1,2-Dichloroethane)--

1,2-dichloroethane is a large-volume chemical (Table 7) that is a bacterial mutagen and a suspected carcinogen (Helmes et al, 1983; Singh et al, 1982). Estimated yearly U.S. emissions exceed 0.2 million tons. It is an exclusively man-made chemical that has also become a part of our global environment. Singh et al (1983b) report a background concentration of about

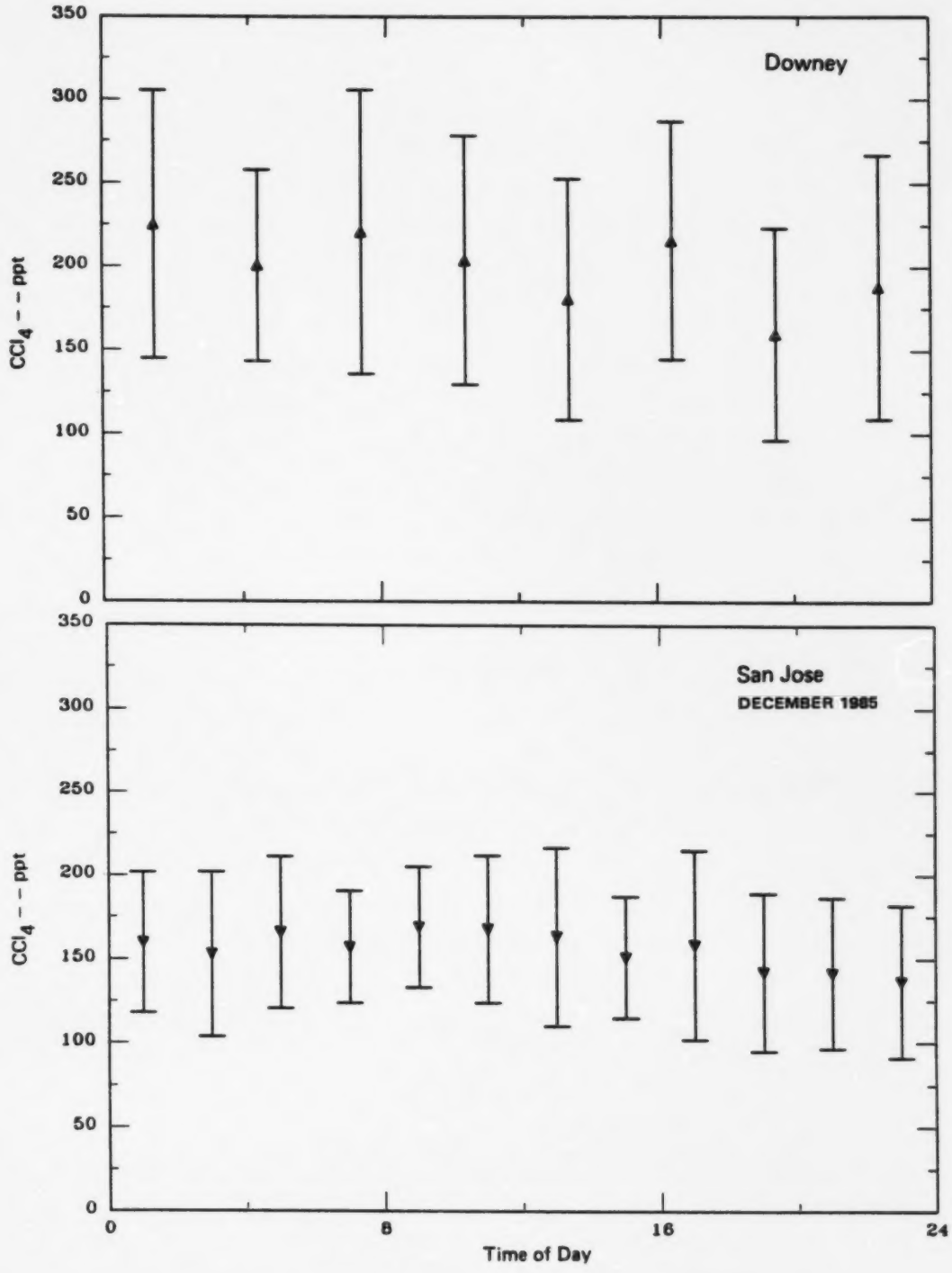

Figure 18. Diurnal behavior of carbon tetrachloride at Downey and San Jose sites.

40 ppt at 40°N (Table 11). It is obvious from Tables 8 through 10 that urban levels are significantly elevated.

The chemical was most abundant at the Houston site where average and maximum concentrations of 0.45 ppb and 2.5 ppb, respectively, were measured. This 0.45 ppb concentration measured in March is significantly lower than the 1.5 ppb average concentration at this site in May 1980 (Singh et al 1983e). In Downey, CA the average concentration was only 0.1 ppb (maximum 0.6 ppb). This is also much lower than the 0.5 ppb average measured in Los Angeles in April 1979. Inquiries at the California Air Resources Board confirmed that several major emitters of 1,2-dichloroethane had closed down during this time. Brodzinsky and Singh (1983) report an average concentration of 0.37 ppb based on available data from cities in the United States. Figure 19 shows the mean diurnal behavior of 1,2-dichloroethane at the Downey, CA site.

Ethylene Dibromide--

1,2-dibromoethane (also commonly known as ethylene dibromide) is a suspected carcinogen (Helmes et al, 1983; Singh et al, 1982). The estimated risk associated with exposure to 1,2-dibromoethane is nearly 50 times the risk from 1,2-dichloroethane for equal exposure (Albert, 1980). About 0.1 million tons of this chemical are manufactured in the United States every year (Table 7). It is primarily used as a gasoline additive and a fumigant. Its atmospheric reactivity is comparable to that of 1,2-dichloroethane (Table 12). Controls have been placed on the use of this chemical in many areas, and it is not an additive used in unleaded gasoline. Its future market, therefore, can be expected to decline. Its average concentration was the highest at the Houston site (0.3 ppb), in part because the site is located close to Interstate Highway 10. Average concentrations were about 0.1 ppb at the Downey and Denver sites, and less than 0.02 ppb at all other locations. Maximum measured concentrations ranged from 0.02 ppb to 3.2 ppb (Tables 8 through 10). If one excludes the Houston site, the maximum concentration is a significantly lower number of 0.6 ppb. These measurements are comparable to the 0.06 ppb average of all urban data reported by Brodzinsky and Singh (1983). Figure 20 shows the measured diurnal distribution of 1,2-dibromoethane at the Downey and Denver sites.

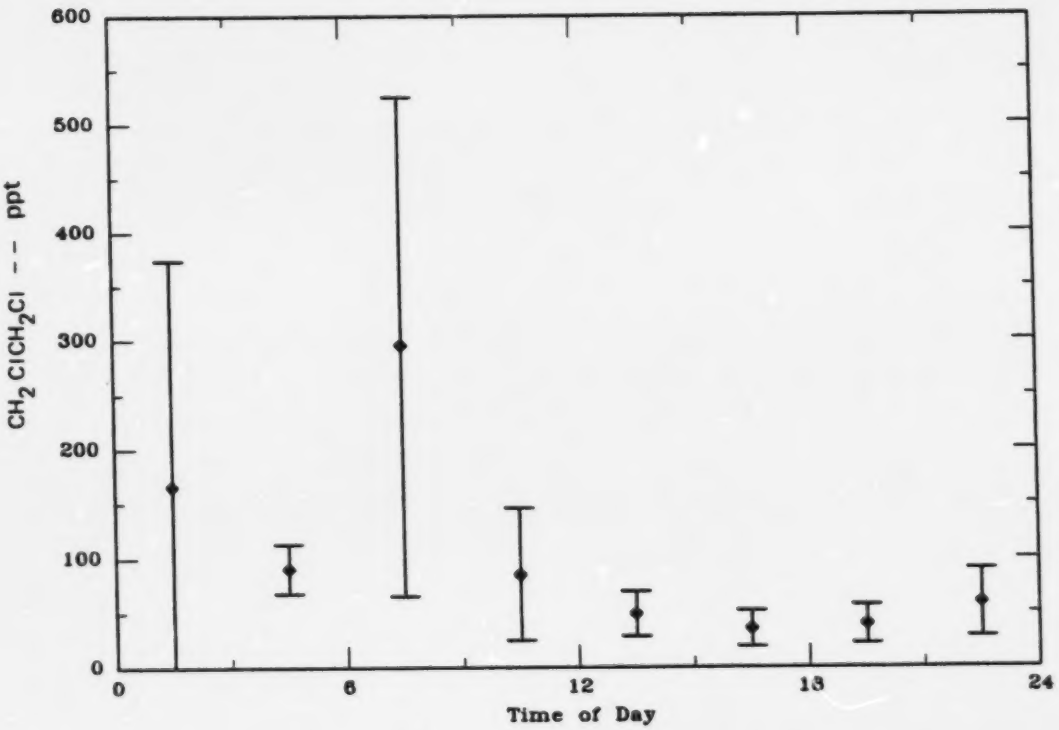

Figure 19. Diurnal behavior of ethylene dichloride at Downey, CA site.

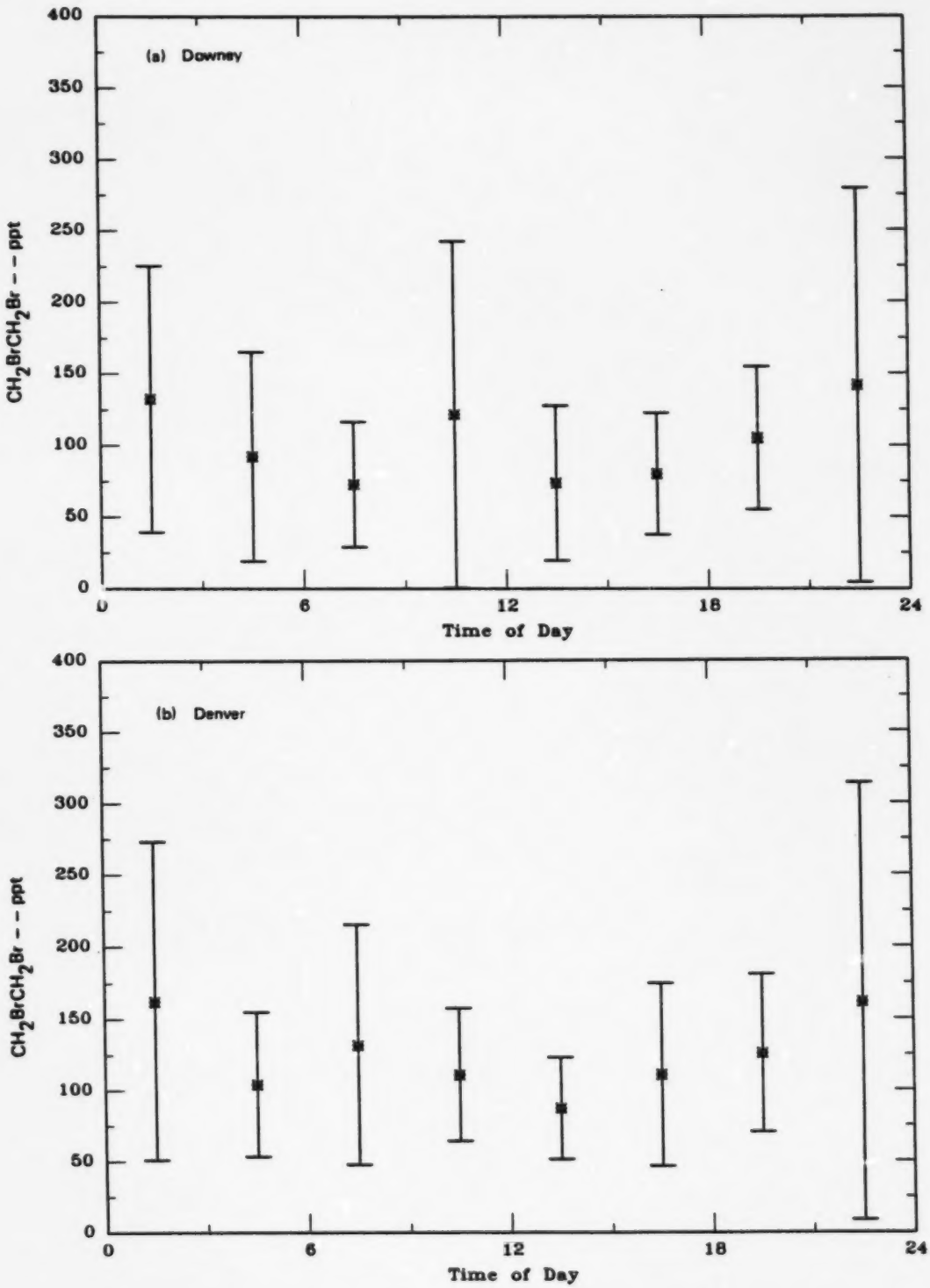

Figure 20. Diurnal behavior of ethylene dibromide at Downey (CA) and Denver sites.

1,1,1-Trichloroethane--

1,1,1-trichloroethane is another large-volume chemical that is released in significant quantities to the atmosphere (Table 7). The chemical has a long atmospheric lifetime and is globally distributed (Singh et al, 1979a,b). Its atmospheric residence time is estimated to be about eight years (Singh, 1979b; Singh et al, 1983b, Prinn et al, 1983); thus about 15 percent of all 1,1,1-trichloroethane released at ground level enters the stratosphere, where it can interact with ozone in a way similar to fluorocarbons. 1,1,1-trichloroethane is suspected to be weakly mutagenic (Helmes et al, 1983), although considerable disagreement on its mutagenic and carcinogenic potential persists (Farber, 1979; Lapp et al, 1979). The background burden of this chemical is constantly increasing; background concentration is now reported to be about 0.2 ppb (Table 11).

Average concentrations at all sites ranged from 0.3 to 1.2 ppb while maximum concentrations ranged from 0.5 to 3.2 ppb. The impact of local meteorology is best demonstrated for the San Jose site. The lowest and the highest average levels were measured at this site during August and December experiments. Stagnant conditions during the winter experiment trapped chemicals to cause a fourfold increase in the abundance of 1,1,1-trichloroethane. It is reasonable to suggest that similar meteorological events at other sites would also result in much elevated concentrations. Brodzinsky and Singh (1983) reported an average from all urban data of 0.85 ppb from measurements available prior to 1981. The present data are well within this range and that of our earlier measurements (Singh et al, 1983e). 1,1,1-trichloroethane acts like an inert chemical for all practical purposes. Its urban distribution is therefore controlled primarily by its emissions and the prevailing meteorological conditions. Figure 21 shows the diurnal behavior of this chemical at San Jose during three different seasons. Figure 22 shows similar behavior at the Philadelphia and Downey sites.

1,2-Dichloropropane--

1,2-dichloropropane, a bacterial mutagen (Helmes et al, 1983) was the only chlorinated propane measured. Its average measured concentration was in the range of 0.02 ppb to 0.16 ppb at all sites. A concentration as high as

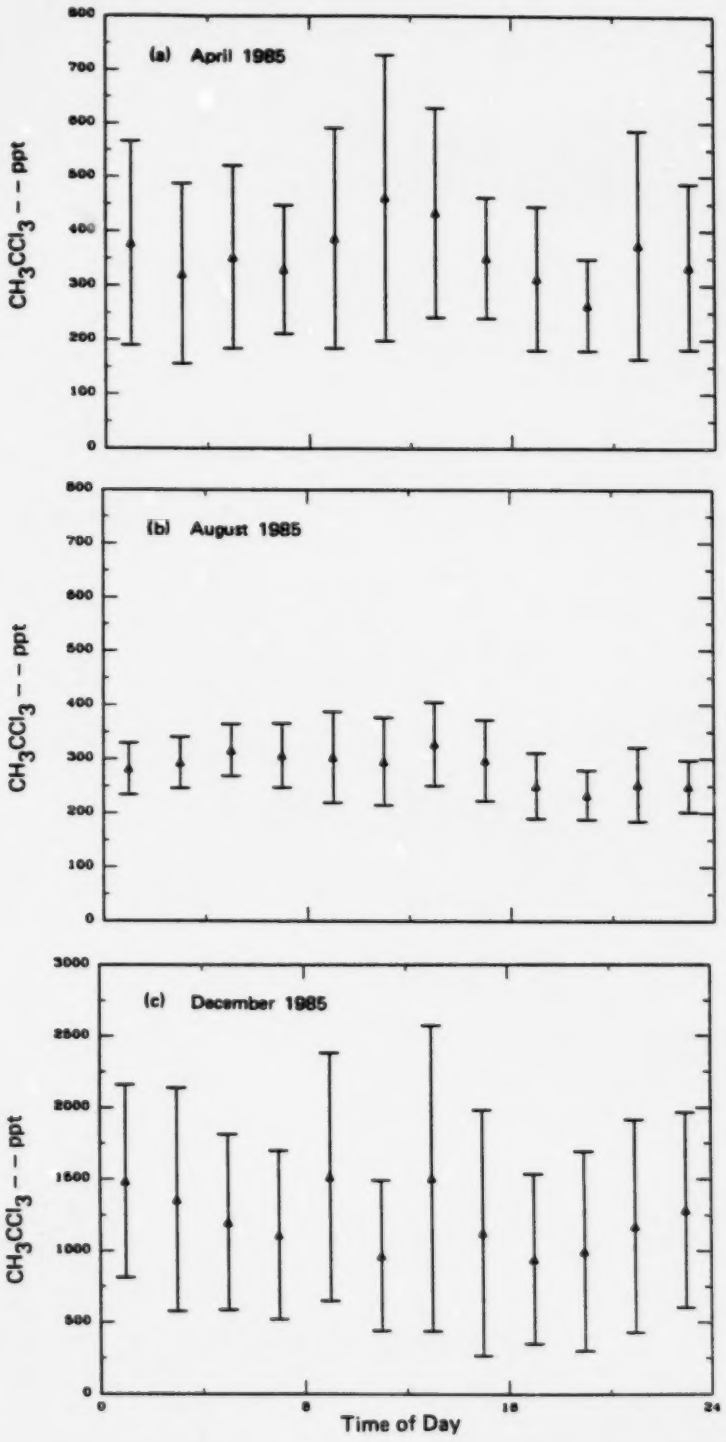

Figure 21. Diurnal behavior of 1,1,1 trichloroethane at San Jose site during April, August, and December 1985.

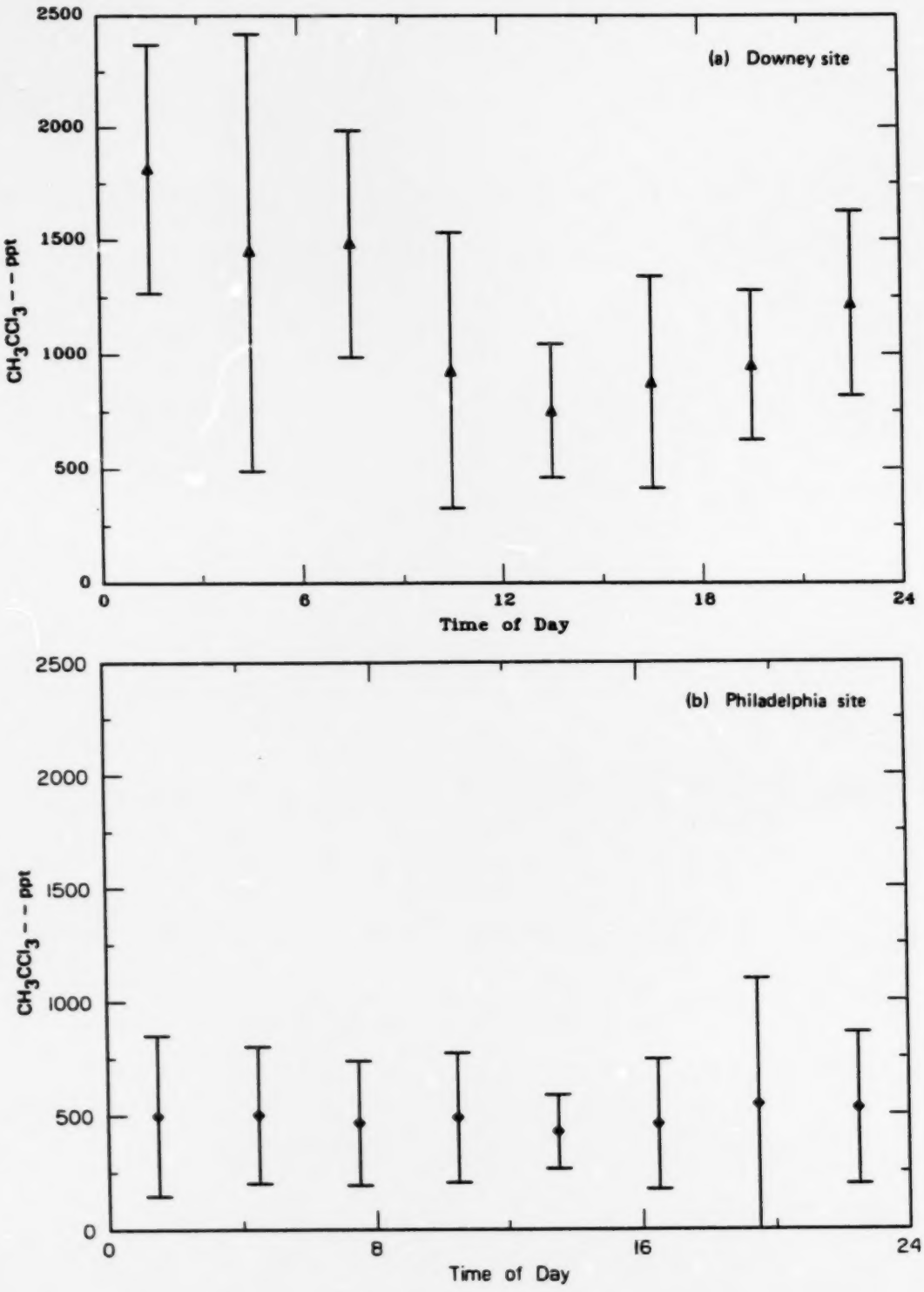

Figure 22. Diurnal behavior of 1,1,1 trichloroethane at Downey (CA) and Philadelphia sites.

0.7 ppb was also measured at Houston. In the San Jose experiments, virtually the lowest average concentrations (0.02 to 0.03 ppb) were encountered. Despite extreme stagnation during the San Jose winter experiment, the abundance of 1,2-dichloropropane registered very little change, suggesting the virtual absence of local sources here. This extremely low abundance is in accord with the data reported by Brodzinsky and Singh (1983). We expect 1,2-dichloropropane to be quite reactive, and estimate that a daily loss rate of about 10 percent occurs (Table 12).

Chloroethylenes

Two chloroethylenes were measured. These were trichloroethylene and tetrachloroethylene, both of which are high volume solvents with annual emissions of 0.15 Tg and 0.37 Tg, respectively, in the United States. Both of these chemicals are mutagens and suspect carcinogens although disagreements on carcinogencity still persists (Albert, 1980; Demopoulos et al, 1980, Greenberg and Parker, 1979, Helmes et al, 1983).

Trichloroethylene--

Trichloroethylene was measured at an average concentration of 0.05 to 0.27 ppb. Maximum concentrations were in the range of 0.25 to 1.0 ppb. The highest average concentration of 0.27 ppb was measured in San Jose during winter under highly stagnant meteorological conditions. Trichloroethylene has been measured by a number of investigators, and Brodzinsky and Singh (1983) report a concentration of 0.5 ppb based on the average of all available urban data. It is a highly reactive chemical, and a daily loss rate of 17 percent is estimated (Table 12). In part, because of its reactivity, a strong diurnal profile is observed. Figure 23 shows the diurnal behavior of this chemical in different seasons at the San Jose site. The background concentration of trichloroethylene is 10-15 ppt, and no natural sources are known to exist. The production of trichloroethylene has declined steadily in the last decade, in part because its emissions are governmentally controlled due to its participation in smog formation.

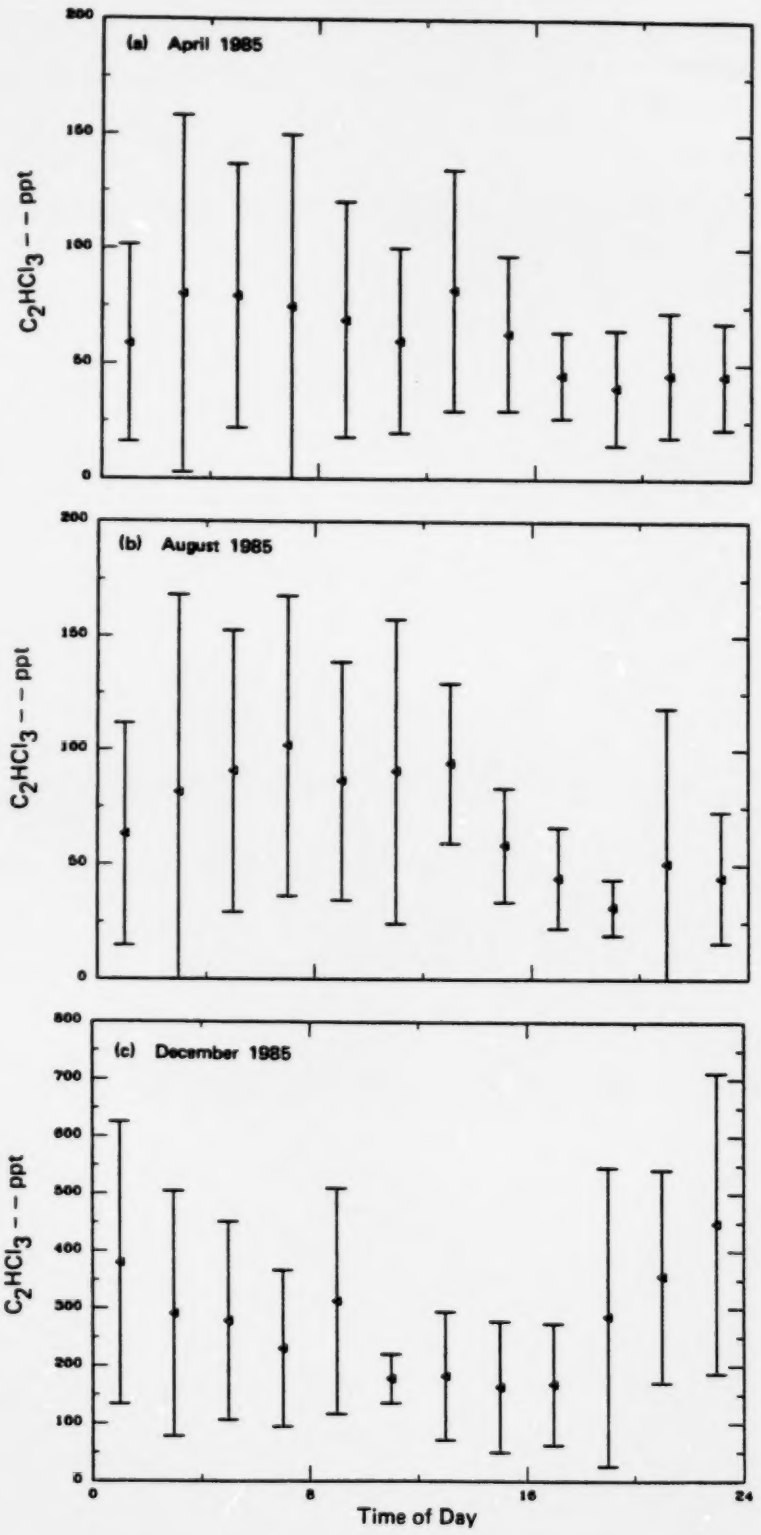

Figure 23. Diurnal behavior of trichloroethylene at San Jose site during April, August, and December 1985.

Tetrachloroethylene--

Unlike trichloroethylene, the reactivity of tetrachloroethylene is modest, and it is unlikely to participate in smog formation (Dimitriades et al, 1983; Singh et al, 1983a). We estimate that less than 2 percent is depleted daily by photochemical reactions. Average concentrations in the range of 0.2-1.9 ppb and maximum concentrations in the range of 0.8-6.6 ppb were measured. The average atmospheric abundance of tetrachloroethylene was 5.6 times that of trichloroethylene although this ratio varied from 2.8 to 8 from site to site. This ratio can be compared to a ratio of 2-4 measured earlier by Singh et al, (1983e). The average concentration measured here (0.2-1.9 ppb) can be compared to a concentration of 0.8 ppb reported by Brodzinsky and Singh (1983) as an average of all available urban data. The three San Jose experiments clearly show the effect of season and meteorology. The average tetrachloroethylene concentration as measured in December during highly stagnant meteorological conditions was seven times that measured in the summer. Figure 24 shows this behavior of tetrachloroethylene at San Jose. For purposes of comparison the mean diurnal behavior of tetrachloroethylene at the Philadelphia, Staten Island, and Downey sites is also shown in Figure 25. It is an exclusively man-made chemical, and no natural sources are known to exist. The urban levels everywhere are significantly above its background concentration of about 50 ppt.

Aromatic Hydrocarbons (AHCs)

Eight important aromatic hydrocarbons were sought. Benzene is a suspected human carcinogen (Helmes et al, 1983; Singh et al, 1982). Carcinogenicity as well as mutagenicity information on toluene is disputed (Albert, 1980), although the compound has been classified as a potential mutagen (U.S.S.G., 1980). In most other cases, toxicity data are currently highly uncertain. In addition, these hydrocarbons are photochemically reactive and contribute to smog as well as to a number of intermediate products that may be additionally toxic. Although aromatic hydrocarbons are manufactured in large quantities, direct releases constitute a small part of the atmospheric emissions.

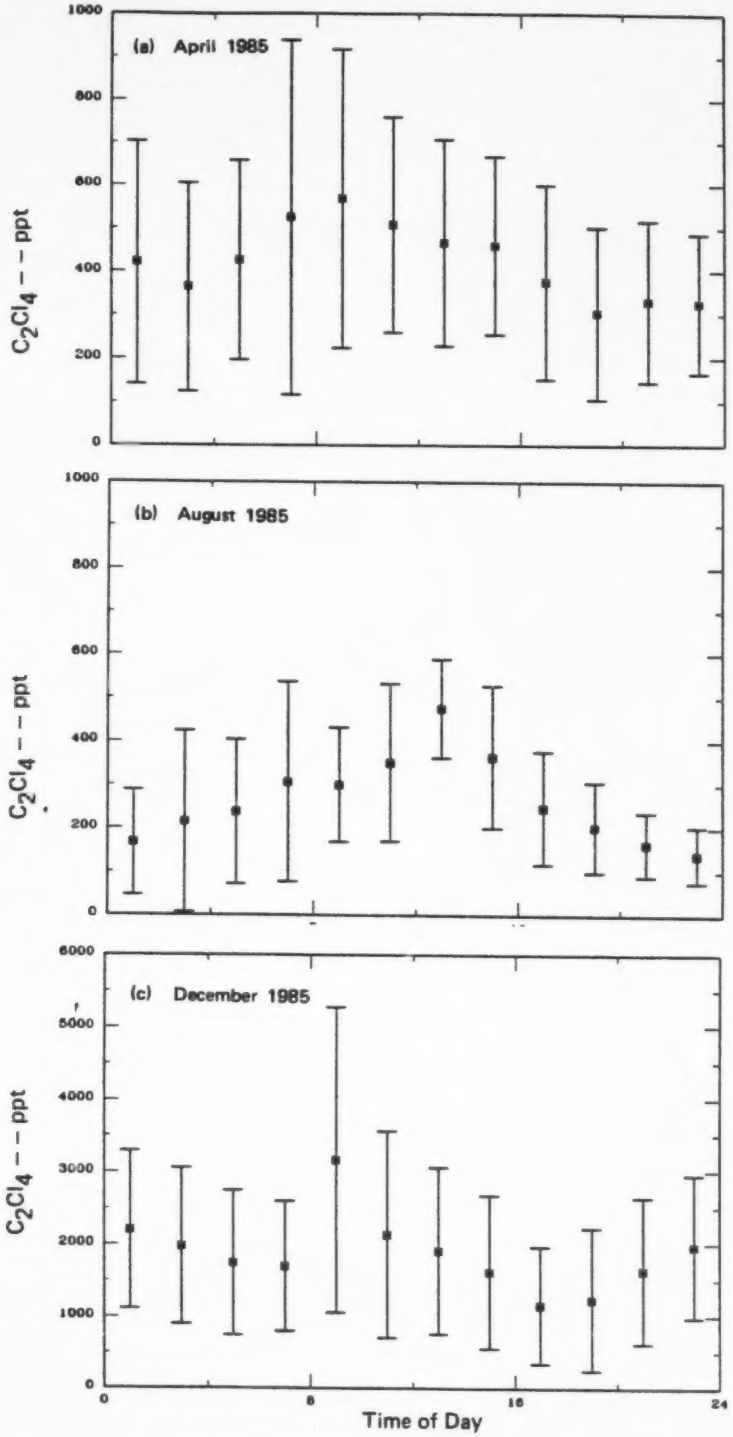

Figure 24. Diurnal behavior of tetrachloroethylene at San Jose site during April, August, and December 1985.

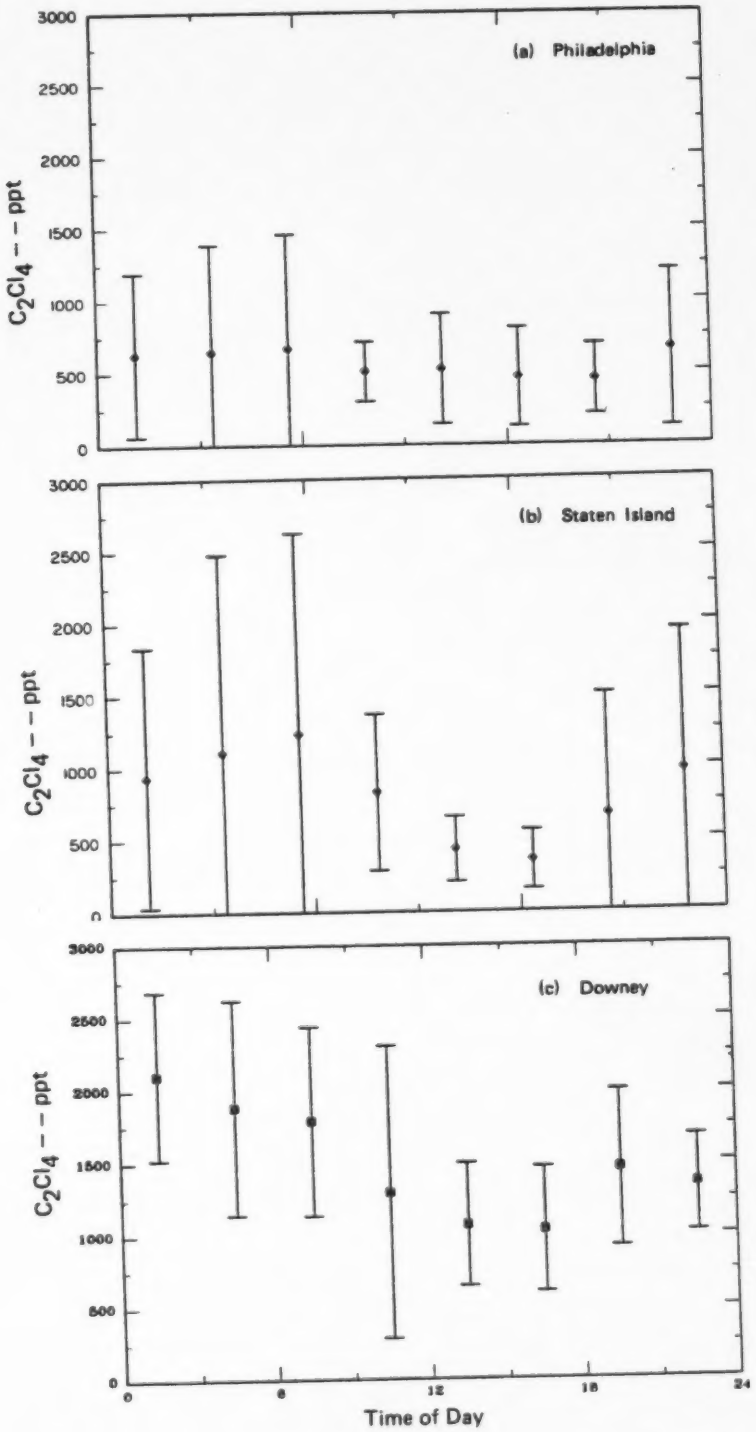

Figure 25. Diurnal behavior of tetrachloroethylene at Philadelphia, Staten Island and Downey (CA) sites.

The dominant ambient source appears to be automobile exhaust. Average concentrations (Tables 8 through 10) in the range of 1.9-12.4 ppb benzene, 3.3-21.2 ppb toluene, 0.8-6.2 ppb ethyl benzene, 1.6-13.1 ppb m/p-xylene, 0.8-5.7 ppb o-xylene, 0.4-4.2 ppb 3/4-ethyl toluene, 0.1-1.3 ppb 1,3,5-trimethyl benzene, and 0.7-5.4 ppb 1,2,4-trimethyl benzene were measured. Maximum concentrations at each site are typically an order of magnitude higher. The two dominant members are toluene and benzene, with toluene nearly twice as abundant as benzene. Together these two species account for more than 50 percent of the abundance of this group. Although variabilities exist in these measurements, the average distribution of aromatic hydrocarbons in urban air as measured from these and our previous data, is benzene 21 percent, toluene 36 percent, ethyl benzene 9 percent, m/p-xylene 15 percent, o-xylene 7 percent, 3/4-ethyl toluene 4 percent, 1,2,4-trimethyl benzene 6 percent, and 1,3,5-trimethyl benzene 2 percent (Singh, et al, 1985b).

One of the primary means of atmospheric removal of AHCs is their reaction with the OH radical. Removal by reaction with ozone, or due to photolysis, can be estimated to be much less than 1 percent of the OH removal rate. The OH reaction rates (cm^3 $molec^{-1}$ s^{-1} at 298°K) have been measured to be 1.2×10^{-12} for benzene (Atkinson et al, 1979; Tully et al, 1981). The relative rate constants compared to benzene (at 298°K) are toluene-4.8, ethyl benzene-6.7, p-xylene-9.2, m-xylene-17.5, o-xylene-10.0, ethyl toluene-11.0, 1,2,4-trimethyl benzene-33.0, and 1,3,5-trimethyl benzene-52.0 (Atkinson et al, 1979). Figure 26 shows a clear example of the diurnal behavior of these AHCs as observed at the Downey site. This site is chosen both for demonstration purposes, and because fair weather prevailed during the entire period of the experiment so that normal urban activities were not interrupted. Figure 26 clearly shows dramatic diurnal variation with minimum late morning and early afternoon concentrations.

The afternoon minimum could be due to a number of reasons including (1) chemical removal, (2) dilution due to the afternoon increase in mixing depth, and (3) reduced emissions. To eliminate the role of dilution, Figure 27 shows the relative mean diurnal behavior of AHCs as normalized against benzene. These relative afternoon minimums show the faster removal of AHCs, as

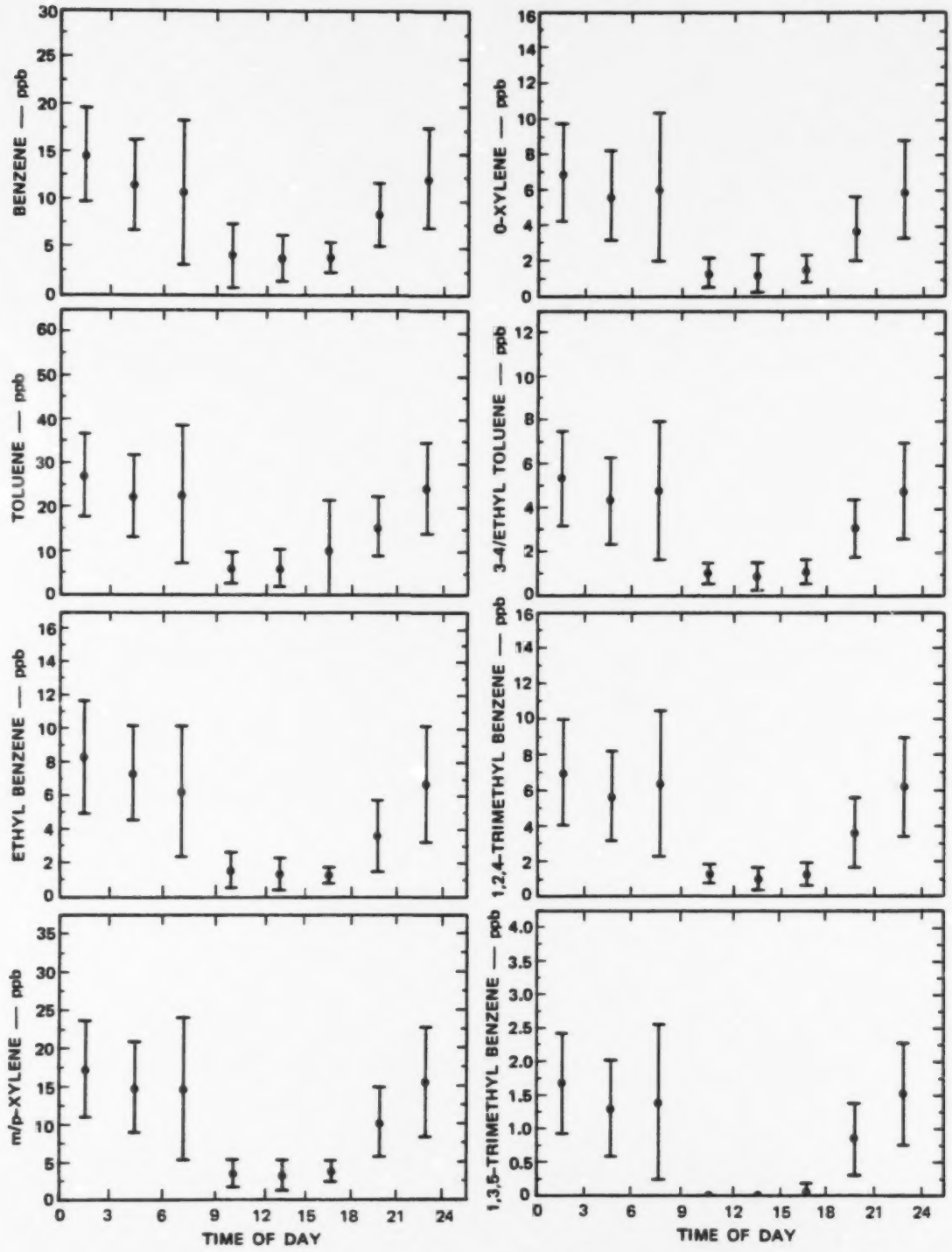

Figure 26. Diurnal behavior of aromatic hydrocarbons in southern California (Downey site).

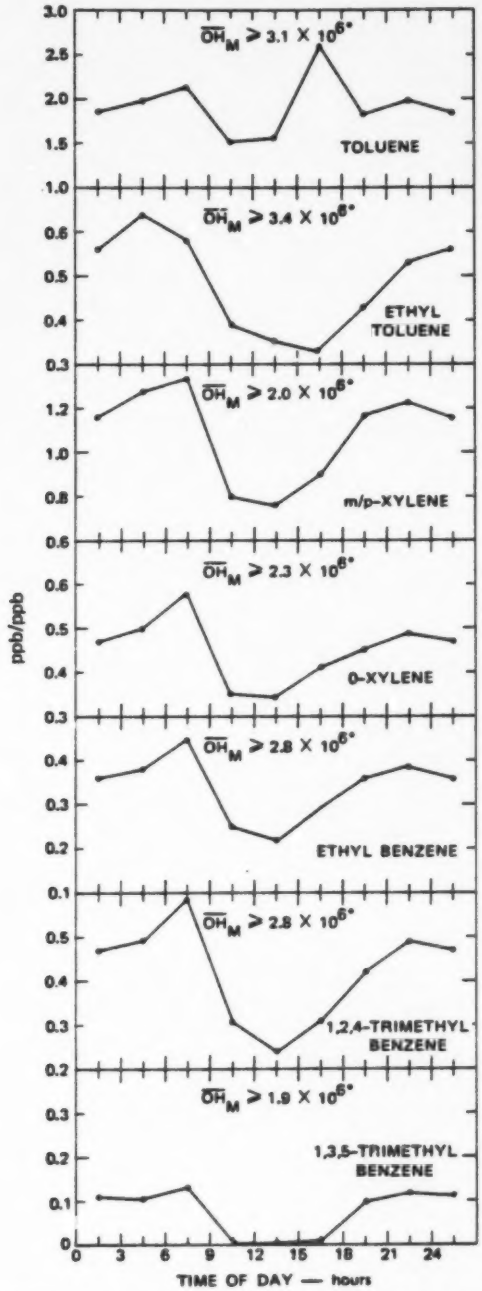

Figure 27. Mean diurnal concentration of aromatic hydrocarbons relative to benzene (ppb/ppb) at Southern California Downey site.

suggested by their greater relative reactivity towards the OH radical. It is further possible to estimate a lower limit of the mean OH radical concentration. This computation is possible if one assumes that the decline in the AHC/benzene ratio between 0600-0900 hrs and 1200-1500 hrs is due strictly to chemical removal. If there were no emissions after the 0600-0900 period, the 1200-1500 hr concentration ratio would probably be somewhat lower. That is why only a lower limit is computed as follows:

$$\overline{OH}_M \geq \frac{1}{tK_b\left(\frac{K_{AHC}}{K_b} - 1\right)} \quad \ell n \left\{ \frac{[AHC]o/[B]o}{[AHC]_t/[B]_t} \right\} \qquad (1)$$

K_{AHC} and K_b are the OH rate constants for AHC and benzene, respectively. The initial time (t = 0) is taken to be 0730, while the final time (t = 6 hrs) is 1330. The minimum OH concentrations required to accomplish the decline in non-benzene AHC concentration are 3.1 x 10^6 (molec cm^{-3}), 3.4 x 10^6, 2.0 x 10^6, 2.3 x 10^6, 2.8 x 10^6, 2.8 x 10^6 and 1.9 x 10^6 for toluene, ethyl benzene, m/p-xylene, o-xylene, 3/4-ethyl toluene, 1,2,4-trimethyl benzene and 1,3,5-trimethyl benzene, respectively. (In the case of m/p-xylene the meta isomer is assumed to be twice as abundant as the para isomer based on data of Mayrsohn et al, 1976.) Thus, a morning average OH concentration of at least 2.6 (± 0.6) x 10^6 molec cm^{-3} was present at Downey, even during the month of February. This is not significantly lower than the summertime OH concentration estimates of 2.5 (± 2.0) x 10^6 molec cm^{-3} (Calvert, 1976) and 2.9 (± 1.9) x 10^6 molec cm^{-3} (Singh et al, 1981b) for this region. Assuming a mean daytime OH abundance of 2.5 x 10^6 molec cm^{-3} (nighttime OH is expected to be negligible in comparison) and the rate constant data provided above, the life time (e-fold) of AHCs in the boundary layer of a typical urban atmosphere can be computed (in units of sunlit hours) to be benzene-93 hrs, toluene-19 hrs, ethyl benzene-14 hrs, p-xylene-10 hrs, m-xylene-5 hrs, o-xylene-9 hrs, ethyl toluene-8 hrs, 1,2,4-trimethyl benzene-3 hrs and 1,3,5-trimethyl benzene-2 hrs. In 10 sunlit hours, 10 percent of benzene, 40 percent of toluene and

nearly 99 percent of 1,3,5-trimethyl benzene could be depleted via reaction with the OH radical alone.

A nearly sixfold difference in the ambient benzene concentrations was observed at the San Jose site during different seasons. Figure 28 shows the diurnal behavior of benzene at this site during April, August, and December. As is typical of many pollutants the highest values for benzene were measured during the night and early morning hours.

The increased demand for high octane rating in unleaded fuels has led to an increase in the aromatic content. In the exhaust, however, the catalytic converter can preferentially reduce the aromatic fraction. Typical results (EPA, 1978) suggest that the AHC fraction is 17 percent in the exhaust of cars with catalyst, and 24 percent in cars without catalyst. Figure 29 shows average benzene and toluene concentrations measured at several sites in Southern California. Because of the possibility of seasonal trends (Shikiya et al, 1984), data taken during winter months is excluded from Figure 21. Further, it should be noted that each data point in Figure 29 represents an average of a large number of samples. The pre-1970 data are taken from Altshuller and Bellar (1961), Lonneman et al, (1968), and Leonard et al, (1976). Subsequent data are taken from this study, the results summarized in Brodzinsky and Singh (1983), and from Shikiya et al, (1984). The Brodzinsky and Singh (1983) study is a comprehensive review of all available volatile organic chemical data for the period of 1970 to 1980. It is clear from Figure 29 that benzene and toluene concentrations have declined dramatically during the last two decades. Since the mid-1970's, however, the rate of decline in benzene concentrations appears to have slowed considerably. It is reasonable to assume that the concentrations of other AHCs have declined similarly over the last two decades.

In recent years, attempts also have been made to measure concentrations of AHC in clean remote atmospheres. Table 13 summarizes some of these data. It is clear from Table 13 that benzene and toluene are the dominant species. Unlike the urban atmosphere, the mean toluene/benzene ratio at mid-latitudes is only 0.3 to 1.0. Assuming an OH radical concentration of 6×10^5 molec cm^{-3} in the clean source, it is possible to compute the residence time of an

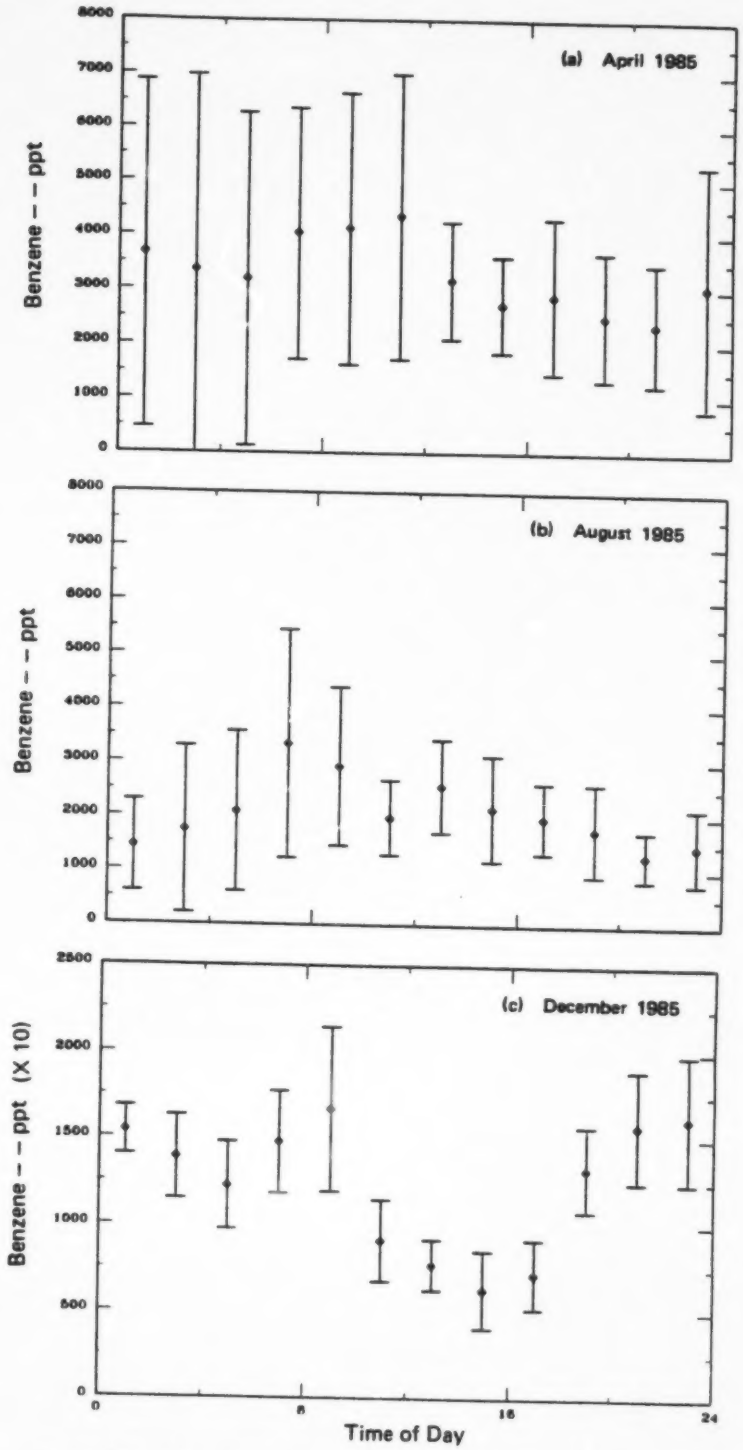

Figure 28. Diurnal behavior of benzene at San Jose site during April, August, and December 1985.

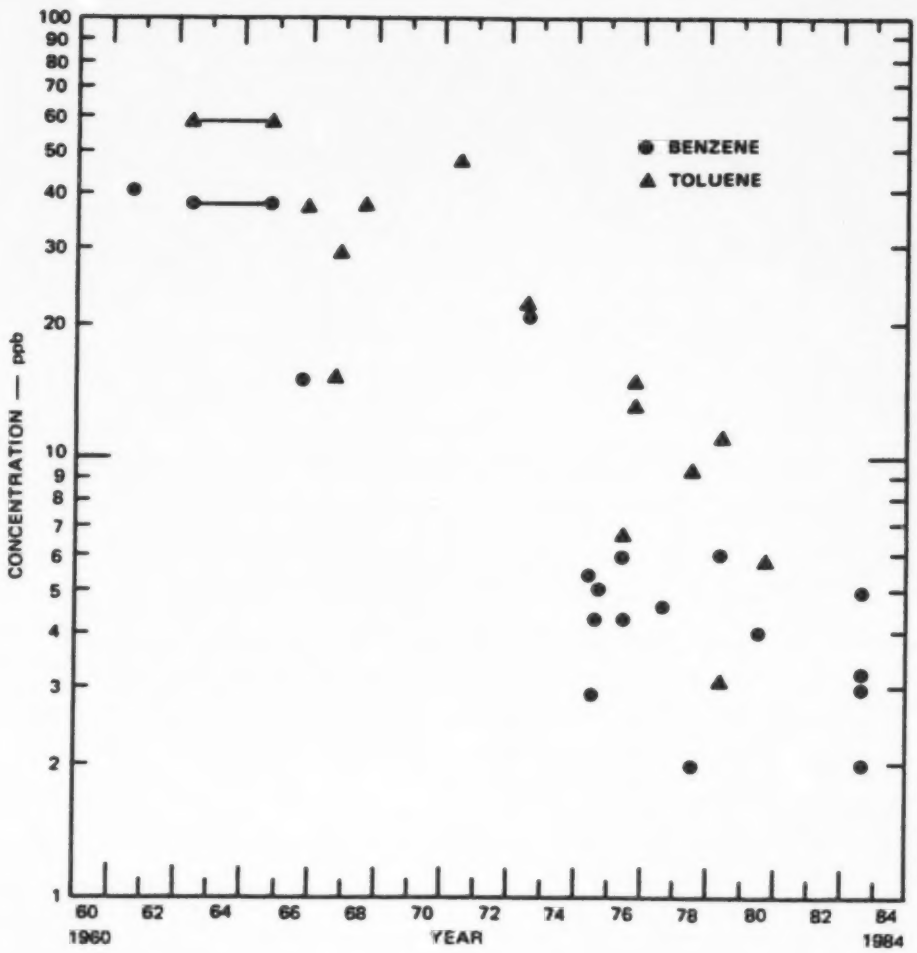

Figure 29. Benzene and toluene trend in the atmosphere of the South Coast Air Basin of California.

TABLE 13. MIDLATITUDE BACKGROUND CONCENTRATIONS OF SOME AROMATIC HYDROCARBONS IN REMOTE MARINE AND CONTINENTAL ATMOSPHERES

Chemical	Location	Average Concentration (ppb)	Source
benzene	Atlantic air (35°N)	0.07 ± 0.03	(1)
	Pacific air (45°N)	0.23 ± 0.04	(2)
	Niwot Ridge* (40°N)	0.24	(3)
	Niwot Ridge (40°N)	0.16 ± 0.08	(4)
	Pacific air (47°N)	0.23 ± 0.11	(5)
	Northern hemisphere	0.05	(5)
	Southern hemisphere	0.01	(5)
toluene	Atlantic air (35°N)	0.02 ± 0.01	(1)
	Pacific Air (45°N)	0.22 ± 0.04	(2)
	Niwot Ridge (40°N)	0.14	(3)
	Niwot Ridge (40°N)	0.13 ± 0.17	(4)
	Pacific air (47°N)	0.13 ± 0.08	(5)
	Northern hemisphere	0.02	(5)
	Southern hemisphere	0.006	(5)
o/m/p-xylenes	Atlantic air (48°N)	0.01 - 0.02	(6)
	Pacific air (40°-0°N)	0.04 - 0.02	(5)
	Indian Ocean (41°S)	0.003 - 0.005	(6)

Source: (1) Penkett (1982); (2) Rasmussen and Khalil (1983); (3) Greenberg and Zimmerman (1984); (4) Roberts et al. (1984); (5) Nutmagul and Cronn (1984); (6) Eichmann et al. (1980).

*Niwot Ridge is located in the Colorado Rockies.

air mass needed to change toluene/benzene ratio from 1.7 to 0.3-1.0. From Equation (1) it is estimated that such an air mass would be only 2 to 7 days away from its source. To date it is not known if significant nonanthropogenic sources of AHCs exist.

Oxygented Species

The oxygenated species, peroxyacetylnitrate (PAN), peroxypropionylnitrate (PPN), formaldehyde, and acetaldehyde were measured. Although these are dominant constituents of the polluted urban atmosphere, they are also an important part of the natural atmosphere and play a key role in the photochemistry of the troposphere (Singh and Hanst, 1981; Low et al, 1981, Singh et al, 1986).

Peroxyacetylnitrate and Peroxypropionylnitrate--

It is evident from Tables 8 through 10 that average PAN concentrations in the range of 0.6 to 1.6 ppb were measured at all sites. Maximum concentrations, typically encountered during daytime, were in the range of 2 to 8 ppb. Figure 30 shows the diurnal behavior of PAN at the Philadelphia, Downey, Houston, and Denver sites. During the field experiment in Denver, PAN concentrations in the 0.5 to 1 ppb were measured during periods of snowfall. Although PPN could be detected, it was present at much lower concentrations. Average concentrations of PPN were in the 0.02 to 0.2 ppb range. Frequently its concentrations were below the detection limit and they never exceeded 1 ppb (Tables 8 and 9). PAN and PPN were not measured during the San Jose experiments. Average PAN/PPN ratio varied between 7 to 30. Figure 31 shows the diurnal behavior of PPN at the Downey, Houston, and Denver sites.

Formaldehyde and Acetaldehyde--

Measurements of aldehydes in polluted atmospheres have received much attention in recent years because of their key involvement in photochemical smog processes as well as their potential toxicity (Lloyd, 1979; Albert, 1980). In the past, ambient measurements of formaldehyde have been performed using the chromotropic acid procedure (Altshuller and McPherson, 1963; U.S. Public Health Service, 1965; Fushimi and Miyaki, 1980) and to a limited extent

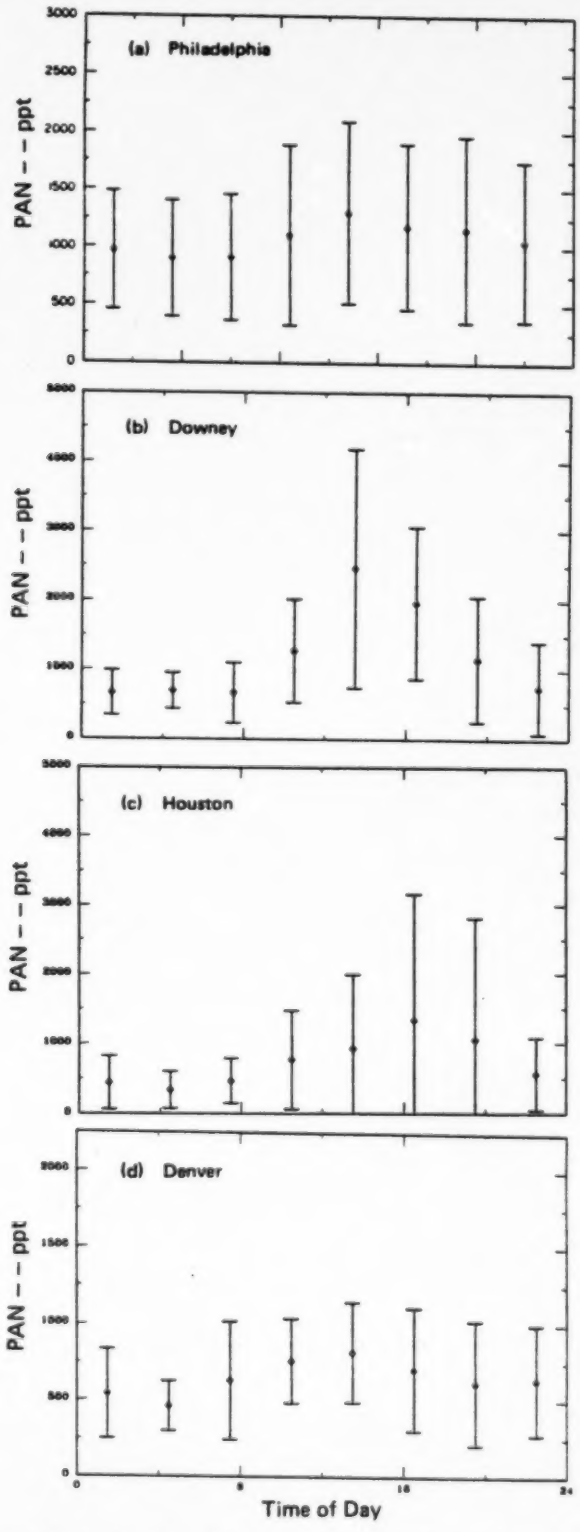

Figure 30. Diurnal behavior of PAN at Philadelphia, Downey (CA), Houston, and Denver sites.

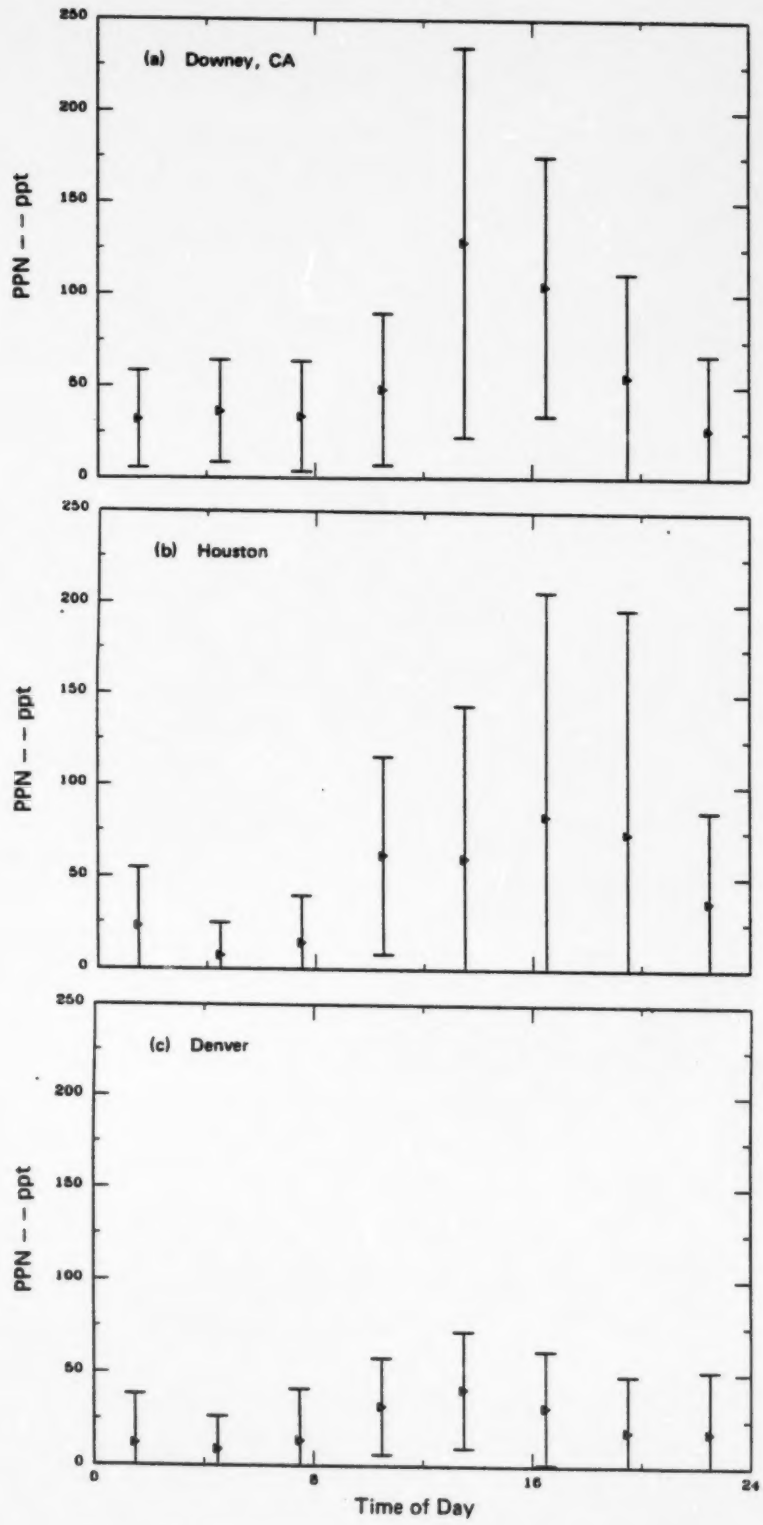

Figure 31. Diurnal behavior of PPN at Downey, Houston, and Denver sites.

by Fourier-transform infrared spectroscopy (Platt et al, 1979; Tuazon et al, 1980). In more recent years aldehydes have been measured by reacting them with 2,4-Dinitrophenylhydrazine (DNPH), followed by the analysis of the resultant-hydrozones by high performance liquid chromotography (Kuwata et al, 1979; Kuntz et al, 1980; Fung and Grosjean, 1981). Ambient aldehyde data collected by the chromotropic acid procedure are of unsure quality (NAS, 1981). To date, the bulk of ambient aldehyde data are available from a few locations such as Southern California (Grosjean 1982); selected northeastern sites (Cleveland et al, 1977; Tanner and Meng, 1984; Schulam et al, 1985) and from Osaka, Japan (Kuwata et al, 1979; 1983). In the present study, we provide additional formaldehyde and acetaldehyde data in summer and winter based on a series of nine short term field experiments conducted in eight cities.

Table 14 provides a summary of ambient formaldehyde measurements at nine sites in the United States. Field studies at the first four sites exclusively employed the chromotropic acid procedure, while at the last five sites the DNPH-HPLC technique was used. Table 14 shows that during the spring-summer period significant levels of formaldehyde (10 to 20 ppb) are present. The last three studies were performed during the winter-spring period. Comparisons at the Denver site clearly show that formaldehyde levels were much lower in early April as compared to June. In the first week of April the weather in Denver was very cold, and was associated with periods of snowfall. Considerable rain was encountered at the Houston site. The weather in Southern California (Downey) was fair prior to and during our experiment, and significant formaldehyde concentrations were indeed measured. However, it does appear that these levels may also be lower than those encountered in the summertime (Grosjean, 1982). Ambient formaldehyde levels were frequently below our detection limit ($\simeq$ 0.4 ppb) during the March Houston and Denver measurements.

Table 15 summarizes the acetaldehyde concentrations as measured by the DNPH-HPLC method. Average acetaldehyde concentrations of 8.5 ppb at the Downey, CA site are significantly higher than the 1-to-2 ppb levels encountered elsewhere. The highest acetaldehyde concentration of 28 ppb was

TABLE 14. AMBIENT FORMALDEHYDE LEVELS FROM SELECTED LOCATIONS

Field Site Description		Measurement Period	Number Of Data Points	Concentration* (ppb)	
City	Site Address			Maximum	Average ±σ
St. Louis, MO	3400 Pershall Rd.	5-7 June 1980	11	18.7	11.3 ± 4.5 ε
Denver, CO	Marion St. and E. 51st	23-24 June 1980	18	28.7	12.3 ± 5.9 ε
Riverside, CA	Big Spring Rd., and Perimeter Rd.	8-10 July 1980	18	41.0	19.0 ± 7.6 ε
Staten Island, NY	Wild Ave. and Victory Blvd.	3-4 April 1981	17	45.9	14.3 ± 9.1 ε
Pittsburgh, PA	Carnegie Mellon Campus	15-16 April 1981	8	28.5	18.5 ± 6.7 +
Chicago, IL	79th St. and Lavandale	27-28 April 1981	5	15.6	11.3 ± 3.8 +
Downey, CA	Rancho Los Amigos Hospital	28 February - 1 March 1984	48	67.7	15.5 ± 11.9
Houston, TX	Mae St. and I-10 Frontage Rd.	18-19 March 1984	11	22.5	3.8 ± 8.3 +/
Denver, CO	Marion St. and E. 51st	1-2 April 1984	21	5.5	2.3 ± 1.8 +/

*Each data point represents approximately a 2-hour average, concentration except in Downey, CA where 1-h average concentrations were measured.

εChromotropic acid method

+DNPH-HPLC method

/Detectable levels measured only 7 times in Houston and 8 times in Denver. The remainder of data were below detectability. Averages and σ are based on measured concentrations only.

TABLE 15. AMBIENT ACETALDEHYDE LEVELS
FROM SELECTED LOCATIONS

Field Site Description		Number of Data Points	Concentration (ppb)	
City	Measurement Period		Maximum	Average ±σ
Pittsburgh, PA	15-16 April 1981	8	2.6	1.4 ± 0 8
Chicago, ILL.	27-28 April 1981	5	3.4	2.1 ± 0.9
Downey, CA	28 February - 1 March 1984	48	28.4	8.5 ± 6.3
Houston, TX	18-19 March 1984	11	6.7	2.2 ± 1.7
Denver, CO	2-4 April 1984	21	2.1	1.0 ± 0.5

also measured at this site. Another important feature of the Downey site is the small formaldehyde to acetaldehyde concentration of 2 compared to a ratio of 5-to-10 at other sites. At Downey nearly 65 percent of HCHO data lie in the 5-to-15 ppb range, while 71 percent of CH_3CHO data fall in the 1-to-10 ppb range. Figure 32 shows the diurnal behavior of these two aldehydes, with highest concentrations encountered at night. This diurnal pattern is contrary to the summertime aldehyde behavior where the maximum concentrations during periods of photochemical smog occurred in the afternoon (Grosjean, 1982).

In remote background environments, HCHO has been measured in the 0.1-to-1 ppb range (Lowe et al, 1981). Methane oxidation reactions suggest a surface background of about 0.4 ppb. No background concentrations of CH_3CHO have been reported. Analysis of PAN and precursor data by Singh et al, (1985a) suggest that under clean conditions ambient CH_3CHO levels of 0.15-to-0.3 ppb may be present. The summertime 10-to-20 ppb HCHO levels measured here are not atypical of other polluted atmospheres (Altshuller and McPherson, 1963; Cleveland et al, 1977; Joshi, 1979; Kuwata et al, 1979, 1983; Grosjean, 1982; Tanner and Meng, 1984; Schulam et al, 1985). Although acetaldehyde measurements are relatively sparse, studies from Japan (Hoshika, 1977; Kuwata et al, 1979, 1983) report average acetaldehyde levels of 1.5-to-10 ppb. Schulam et al, (1985) find that in Schenectady, N.Y., the bulk of CH_3CHO data were in the 0-to-1 ppb range, and its concentrations never exceeded 5 ppb. High acetaldehyde concentrations in the 2-to-40 ppb range have also been reported from sites in Southern California (Grosjean, 1982).

In the past it has been reported that in the automobile exhaust 65 to 75 percent (by volume) of all aldehydes is HCHO while 7 to 10 percent is CH_3CHO (NAS, 1976). It now appears that this ratio may be strongly altered in favor of CH_3CHO in cars equipped with catalyst converters (NAS, 1981). In addition, significant stationary source emissions can also exist. In the south coast air basin of California, HCHO and CH_3CHO total emissions of 20 metric tons/day and 17 metric tons/day have been estimated. Assuming comparable removal rates, an HCHO/CH_3CHO concentration ratio of 1.7 to 1 would result. Needless to say, the sources of these aldehydes are varied, and their emissions in many urban centers are significantly different from the south coast air basin.

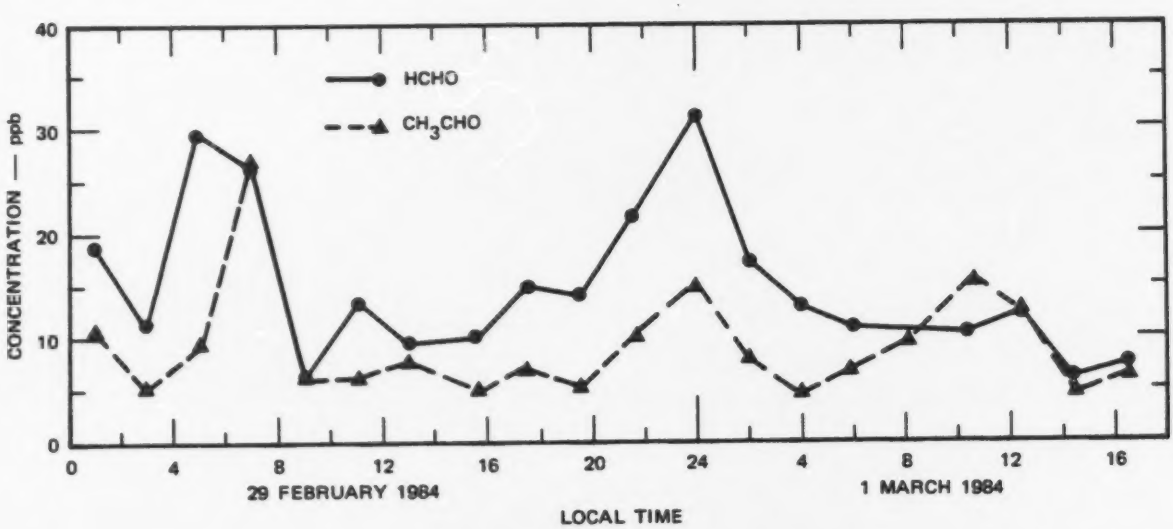

Figure 32. Diurnal behavior of formaldehyde and acetaldehyde concentrations in Southern California (Downey, CA, Site).

While primary emissions contribute to the atmospheric burden of these aldehydes, both chemicals are also formed as secondary pollutants by the atmospheric transformation of common hydrocarbons.

SECTION 6
TRENDS AND SEASONAL CYCLES

Because of the source complexity and wide variations in meteorological parameters, short term experiments such as those performed here are not suitable for establishing long term trends. Table 16 shows the mean concentrations of selected anthropogenic species as measured at the San Jose site during April, August, and December. During the December experiment, a high pressure system blanketed the area pushing carbon monoxide levels to 14 ppm (the highest in five years). A mixing depth of less than 20 meters was frequently encountered. Although emissions of these chemicals probably vary seasonally, there is every indication that this is a small change compared to the effect of the meteorological parameters observed during the December experiment. This four-to-six fold increase implies local sources and a shallow mixed layer. For chemicals like carbon tetrachloride, where little or no local sources may exist, the atmospheric levels are nearly invariant. Further analysis is needed to establish the relationship between ambient levels and meteorological conditions. It is not possible from this data to conclude that winter levels in San Jose are typically higher than summer levels. To the extent that the boundary layer is deeper during summer, it is reasonable to assume that reduced summer levels (Table 16) may prevail. Superimposed on the meteorological conditions are variations in emissions (which are also not known for any given city) and chemical removal processes.

Table 17 also shows data from four cities which were revisited after a number of years. One can conclude that the levels of methylene chloride and trichloroethylene have perhaps declined over the last four to five years. Once again, no definitive seasonal or long-term trends can be established without a clear knowledge of the emissions and meteorological conditions. While detailed meteorological analysis is beyond the scope of this study, it may be possible to analyze these data in the future in the context of prevailing meteorology. Any attempt to estimate human exposure from these measurements must also employ meteorological analysis for temporal extrapolation.

TABLE 16. MEAN AMBIENT CONCENTRATIONS OF SELECTED CHEMICALS AT THE SAN JOSE SITE DURING APRIL, AUGUST, AND DECEMBER 1985

Chemical	Concentration (PPTV)		
	April 1985	August 1985	December 1985
Florocarbon 12	1020	881	1435
Methylene Chloride	1534	1119	4181
Carbon Tetrachloride	193	144	155
1,1,1 Trichloroethane	360	283	1219
Trichloroethylene	63	68	271
Tetrachloroethylene	427	264	1858
Benzene	3296	2060	12372
Toluene	5667	3904	21155

Table 17: MEAN AMBIENT CONCENTRATIONS (pptv) OF SELECT CHEMICALS BASED ON REVISITS IN DIFFERENT SEASONS AND YEARS

Chemical	Staten Island		Los Angeles/Downey		Houston		Denver	
	March/April 1981	April/May 1983	April 1979	February 1984	May 1980	March 1984	June 1980	March/April 1984
Fluorocarbon	512*	566	-	1183	897	512	1005	648
Methylene Chloride	1605	1109	3751	2399	574	324	967	569
Carbon Tetrachloride	309	387	215	199	404	291	174	264
1,1,1 Trichloroethane	468	403	1028	1161	353	375	713	647
Trichloroethylene	167	164	399	184	144	61	198	53
Tetrachloroethylene	292	792	1480	1471	401	169	394	434
Benzene	4204	4367	6040	8720	5780	6130	4390	2230
Toluene	8975	7436	11720	16890	10330	7270	6240	3340

*Concentrations in PPTV (10^{-12} V/V)

SECTION 7

SUMMARY AND CONCLUSIONS

Eight field studies in six United States cities were completed during this program. Twenty nine chemicals, many of which are bacterial mutagens and suspect carcinogens, were measured on a round the clock schedule with the help of an instrumented mobile laboratory. All chemical analyses were performed on-site and in real time. The chemical categories targeted for field measurements included chlorofluoromethanes, halomethanes, haloethanes, chloropropane, chloroethylenes, aromatic hydrocarbons, organic nitrates, and aldehydes.

The ambient analysis of these species was possible with the help of electron capture gas chromatography for the halogenated and nitrogenated species, flame ionization gas chromatography for hydrocarbons, and high-performance liquid chromatography for aldehydes. Eight field experiments were performed in the following six cities:

- Philadelphia, Pennsylvania (one experiment; 4-20 April 1983)
- Staten Island, New York (one experiment; 25 April-1 May 1983)
- Downey, California (one experiment; 18-27 February 1984)
- Houston, Texas (one experiment; 9-17 March 1984)
- Denver, Colorado (one experiment, 24 March-1 April 1984)
- San Jose, California (three experiments; 4-16 April 1985; 12-24 August 1985; 13-21 December 1985)

Although these studies were of short-term duration, our practice of around-the-clock operation allowed for extensive data collection. The degree of temporal and spatial variability in the atmospheric abundance of toxic chemicals is clear from data presented. Typical concentrations of most chemicals measured were in the sub-ppb range, with the exception of aromatic hydrocarbons and formaldehyde (where average concentrations in the 1-to-25 ppb range were encountered). For most predominantly man-made chemicals, average concentrations in urban atmospheres were one-to-two orders of magnitude higher than in clean remote atmospheres.

Meteorology appeared to play a strong role in the average abundance as well as in the diurnal behavior of these chemicals. Typical diurnal profiles showed highest concentrations in the night and early morning hours and minimum values in the afternoon, probably due to deep vertical mixing at this time. The diurnal patterns in San Jose were somewhat different but they also clearly showed the effect of meteorology on the abundance of chemicals. Mean concentrations under severe stagnant conditions encountered at San Jose rose to 4-to-7 times normal values. Ambient data suggest that aldehydes are significantly less abundant in winter compared to summer months. Interpretation of aromatic hydrocarbon data in Southern California showed that the prevailing hydroxyl radical concentrations of 2.6×10^6 molec. cm^{-3} in February are not significantly different from values computed for summer. This is in apparent contradiction to a commonly made assumption that winter hydroxyl levels are much lower. Analysis of historic data further suggests that the concentrations of benzene (the dominant toxic chemical in ambient air) and other aromatic hydrocarbons have declined by a factor of about 10 in the ambient air of Southern California over the last two decades.

Many organic chemicals that are also mutagens are sufficiently long-lived to have distributed themselves globally. Carbon tetrachloride, methylene chloride and tetrachloroethylene are some of the examples. Methyl halides appear to be a group of naturally occurring mutagens that are also globally distributed.

On the whole, we conclude that typical urban atmospheres contain chemicals that are known to be toxic at much higher concentrations. The risks associated with exposure to ambient levels of these species are highly uncertain. The task of characterizing the atmosphere, with which this study is most concerned, is itself, at best, highly incomplete. Much more atmospheric and toxicity data will be needed to determine the risks associated with long-term exposures to low levels of toxic species.

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